I. THE RATE AND MECHANISM OF THE VAPOR-PHASE REACTION BETWEEN WATER AND PARTS-PER-MILLION CONCENTRATIONS OF NITROGEN DIOXIDE.

II. THE RATE AND MECHANISM OF THE AIR OXIDATION OF PARTS-PER-MILLION CONCENTRATIONS OF NITRIC OXIDE IN THE PRESENCE OF WATER VAPOR

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ABSTRACT

Part I

A study of the thermal reaction of water vapor and parts-per-million concentrations of nitrogen dioxide was carried out at ambient temperature and at atmospheric pressure. Nitric oxide and nitric acid vapor were the principal products. The initial rate of disappearance of nitrogen dioxide was first order with respect to water vapor and second order with respect to nitrogen dioxide. An initial third-order rate constant of $5.50\ (\pm\ 0.29) \times 10^4$ liter^2 mole^{-2} sec^{-1} was found at 25°C. The rate of reaction decreased with increasing temperature. In the temperature range of 25° to 50°C, an activation energy of -978 ($\pm$ 20) calories was found.

The reaction did not go to completion. From measurements as the reaction approached equilibrium, the free energy of nitric acid vapor was calculated. This value was -18.58 ($\pm$ 0.04) kilocalories at 25°C.

The initial rate of reaction was unaffected by the presence of oxygen and was retarded by the presence of nitric oxide. There were no appreciable effects due to the surface of the reactor. Nitric oxide and nitrogen dioxide were monitored by gas chromatography during the reaction.

ABSTRACT (contd.)

Part II

The air oxidation of nitric oxide, and the oxidation of nitric oxide in the presence of water vapor, were studied in a glass reactor at ambient temperatures and at atmospheric pressure. The concentration of nitric oxide was less than 100 parts-per-million. The concentration of nitrogen dioxide was monitored by gas chromatography during the reaction.

For the dry oxidation, the third-order rate constant was 1.46 ($\pm$ 0.03) x 10^4 liter^2 mole^{-2} sec^{-1} at 25°C. The activation energy, obtained from measurements between 25° and 50°C, was -1.197 ($\pm$ 0.02) kilocalories.

The presence of water vapor during the oxidation caused the formation of nitrous acid vapor when nitric oxide, nitrogen dioxide and water vapor combined. By measuring the difference between the concentrations of nitrogen dioxide during the wet and dry oxidations, the rate of formation of nitrous acid vapor was found. The third-order rate constant for the formation of nitrous acid vapor was equal to 1.5 ($\pm$ 0.5) x10^5 liter^2 mole^{-2} sec^{-1} at 40°C. The reaction rate did not change measurably when the temperature was increased to 50°C. The formation of nitric acid vapor was prevented by keeping the concentration of nitrogen dioxide low.

Surface effects were appreciable for the wet tests. Below 35°C, the rate of appearance of nitrogen dioxide

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increased with increasing surface. Above 40°C, the effect of surface was small.

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Part 1

The Rate and Mechanism of the Vapor-Phase Reaction Between Water and Parts-Per-Million Concentrations of Nitrogen Dioxide

I. INTRODUCTION

In 1947, A. J. Haagen-Smit noted that smog in Los Angeles was caused principally by a photochemical interaction between oxides of nitrogen and hydrocarbons. Since then, emissions of hydrocarbons into the air from industry and the automobile have largely been controlled. Emissions of the oxides of nitrogen have not been controlled, due mainly to the lack of technology available to remove or prevent the formation of the oxides from burners and engines. Prevention of these emissions is vitally important because nitrogen dioxide in the atmosphere is involved in a photochemical mechanism which initiates the formation of smog.

The primary means of removing nitrogen dioxide from a gas is by absorption in aqueous solutions. The complete mechanism of absorption is not well understood. The process involves gas-phase and liquid-phase reactions as well as the diffusion of products and reactants to and from the two-phase boundary. Overall, nitrogen dioxide in the gas phase reacts with water to form aqueous nitric acid. Nitric oxide is a gas-phase by-product of the reaction. Knowledge of the rates of the gas-phase reactions alone is needed to clarify the roles of the reactions in each phase of the absorption process. In particular, the gas-phase reaction of nitrogen dioxide with water vapor has not been studied in the absence of a liquid phase. As a result, there is confusion relative to the part this reaction plays in the

absorption. To determine the importance of the reaction of nitrogen dioxide with water in the vapor phase, a study was made in which the rate of reaction was measured, and a reaction mechanism was proposed. The influence of oxygen on the reaction was studied. A homogeneous gas-phase system was ensured by measuring the reaction kinetics at part-per-million concentrations of nitrogen dioxide. Other studies which attempted to observe the gas-phase reaction were unsuccessful in that a two-phase system occurred spontaneously as the concentration of nitric acid in the vapor phase increased[17]. The threshhold of the two-phase region is estimated as about 50 ppm at atmospheric pressure and ambient temperature. In the present work, the concentration of nitric acid vapor did not exceed 17 ppm.

II. LITERATURE

The gas-phase reaction of nitrogen dioxide with water vapor has not been studied in detail[7,10,17,19,23]. The overall reaction in both the gas and aqueous phases is

$$3NO_2 + H_2O = NO + 2HNO_3 \quad .$$

Generally, studies involving the two reactants have been concerned with the kinetics of the absorption of nitrogen dioxide into aqueous solutions. A few attempts have been made to study the gas-phase reaction in the absence of an aqueous phase. In each case, a mist or condensate appeared in the reacting system.

A. The Gas-Phase Reaction of Nitrogen Dioxide with Water

Goyer[17] studied the gas-phase reaction of nitrogen dioxide with water photometrically. He reported that, at concentrations of nitrogen dioxide between 0.08 and 8.42 percent by volume (3.46×10^{-5} to 3.51×10^{-3} moles liter^{-1}), the reaction was very fast. When the contact time for one run was doubled (from 12 to 24 seconds), no noticeable change in composition was observed. The presence of nitric oxide severely decreased the extent of reaction. This behavior was attributed to the reverse reaction,

$$NO + 2HNO_3 = 3NO_2 + H_2O \quad .$$

The emphasis of Goyer's work was centered on the formation and nucleation of nitric acid mists which were produced from

the homogeneous gas-phase system. The mist was always present in his system. It was formed by the presence of water and nitric acid in the gas phase. The gas-phase reaction supplies nitric acid nuclei when the partial pressure of the acid exceeds its vapor pressure. Water vapor readily condenses on each nucleus to form strong nitric acid droplets. From his experiments, Goyer concluded that both gas- and liquid-phase reactions occur in the two-phase system.

Christini[10] found that a mist formed when nitric oxide and wet air were allowed to react. The reaction mixture included about 10 percent each of nitric oxide and water vapor, and about 16 percent oxygen, nitrogen accounting for the balance. His studies took place at 50°C and at atmospheric pressure. The mist was collected and found to contain nitric acid and water with a small amount of nitrous acid. Typically, the mist contained about 55 percent nitric acid and 0.1 percent nitrous acid. Christini concluded that nitric acid vapor was formed by a homogeneous gas-phase reaction and suggested the following mechanism:

$$2NO_2 = N_2O_4$$

$$N_2O_4 = NO + NO_3$$

$$NO_2 + NO_3 = N_2O_5$$

$$N_2O_5 + H_2O = 2HNO_3 \quad .$$

The rate of reaction was not studied experimentally. The rapid appearance of the mist when nitrogen dioxide and water vapor alone were allowed to react suggested that the reaction to form nitric acid vapor was fast relative to the oxidation of nitric oxide.

Cathala and Weinreich[7] studied the direct gas-phase reaction of nitrogen dioxide, oxygen and water to form nitric acid:

$$4NO_2 + 2H_2O + O_2 = 4HNO_3 \quad .$$

When they used stoichiometric amounts of each reactant (0.094 atm oxygen, 0.188 atm water vapor and 0.363 atm nitrogen dioxide), a condensate formed which consisted of dilute nitric acid. The rate of reaction was not studied.

Kuzminikh and Udintseva[23] failed to observe a gas-phase reaction when nitrogen dioxide and water vapor were mixed. They attempted to measure the pressure change which should occur in a constant-volume system according to the overall reaction

$$3NO_2 + H_2O = NO + 2HNO_3 \quad .$$

If the reaction were complete, the pressure would be reduced by 25 percent. Harris[19] performed a similar experiment and also observed no reaction. He could detect no mist or condensate when nitrogen dioxide and water vapor were mixed. Simon[32] also combined nitrogen dioxide and water in the gas phase. He analyzed the resulting gases for nitric oxide

by a wet chemical method. No nitric oxide was found, and no mist was formed in the absence of an aqueous phase.

The nature of the gas-phase interaction of nitrogen dioxide and water vapor is poorly understood. The position of the thermodynamic equilibrium for the gas-phase reaction is unfavorable at ambient temperature and pressure, even when the partial pressure of nitrogen dioxide is high. A two-phase system is formed spontaneously, however, forming droplets of dilute nitric acid. The overall reaction,

$$3NO_2(g) + H_2O(g) = NO(g) + 2HNO_3(aq) \quad ,$$

is favored thermodynamically at ambient conditions. If the two-phase system is prevented by keeping the concentration of nitrogen dioxide or water vapor very low, the gas-phase reaction occurs only to a very limited extent. Increasing temperature decreases the extent of reaction. These characteristics--and the problems associated with mixing known concentrations of water vapor--may explain the difficulties encountered by Kuzminykh[23] and Harris[19].

B. The Absorption of Nitrogen Dioxide into Aqueous Solution

Several studies involving the absorption of nitrogen dioxide into aqueous solutions have suggested that the primary reactions in the two-phase problem occur in the vapor phase. The mechanism of absorption has been studied extensively, but is still subject to controversy.

Most studies show that the rate of absorption of nitrogen dioxide is proportional to the concentration of the dimer of nitrogen dioxide, N_2O_4 (dinitrogen tetroxide). Denbigh and Prince[12] studied the absorption of nitrogen dioxide in a wetted-wall column. The rate of absorption was directly proportional to the concentration of N_2O_4 in the gas phase. They suggested that this behavior could be explained by homogeneous reactions in either the gas or the aqueous phase. Caudle and Denbigh[8] made further measurements on wetted-wall columns, measuring the concentration of nitrogen dioxide in the exit gas photometrically. They concluded that the overall reactions,

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

$$NO + NO_2 + H_2O = 2HNO_2 \quad ,$$

occurred entirely at the gas-liquid interface, and only to a minor degree in the bulk phases.

Wendel and Pigford[36] studied the absorption of nitrogen dioxide in a wetted-wall column. The overall rate was controlled by the rate of hydrolysis of N_2O_4:

$$N_2O_4(aq) + H_2O = HNO_2(aq) + HNO_3(aq) \quad .$$

They reported a value of 290 sec^{-1} for the pseudo--first-order rate constant for the reaction. Carberry[6] suggested that the hydrolysis of N_2O_4 was an ionic reaction in solution. He contended that a gas-phase reaction of nitrogen

dioxide with water vapor would be unlikely since gas-phase reactions are in general not ionic in character.

Dekker[11] reported that the rate of absorption was limited by the liquid film resistance. He assumed the following mechanism for the absorption process. Nitrogen dioxide and N_2O_4 diffuse from the bulk gas to the gas-liquid interface. Only N_2O_4 dissolves in the liquid. It then diffuses through the liquid film and reacts rapidly according to the reaction

$$N_2O_4(aq) + H_2O = HNO_2(aq) + HNO_3(aq) \quad .$$

Using a wetted-wall column and analyzing for nitrogen dioxide photometrically, he found that the absorption rates were lower than would be the case if only diffusion in the gas phase were controlling. Dekker noted that the gas-film resistance would be predominant at high concentrations of nitrogen dioxide. As the concentration of nitrogen dioxide in the gas phase decreased, the main resistance to mass transfer would shift towards the liquid phase.

Chambers and Sherwood[9] studied the absorption of nitrogen dioxide into both alkaline and acid solutions in a wetted-wall tower. They reported that the rate was largely limited by the gas-film resistance to transfer of nitrogen dioxide to the liquid phase. In addition, they suggested that a mist of nitric acid, formed by a homogeneous gas-phase reaction, inhibited the diffusion of nitrogen dioxide.

Peters, Ross and Klein[28] found that the rate of the gas-phase reaction as well as the gas-film resistance controlled the rate of absorption. Using a bubble-cap plate absorbing apparatus, they measured the absorption of nitrogen dioxide photometrically. They contended that if absorption were limited alone by diffusion of nitrogen dioxide and N_2O_4 into aqueous solution, the rate of absorption would be proportional to the concentration of nitrogen dioxide rather than proportional to its dimer.

The discussion of the gas-phase reaction in the two-phase system has been centered on the occurrence of a mist when nitrogen dioxide and water vapor come together, and on the presence of nitric oxide in exit gases when alkaline solutions are used as the absorbing medium. In the latter case, nitrous acid formed by the hydrolysis of N_2O_4 should be neutralized according to the reactions

$$N_2O_4(aq) + H_2O = HNO_2(aq) + HNO_3(aq)$$

$$HNO_2 + NaOH = NaNO_2 + H_2O$$

$$HNO_3 + NaOH = NaNO_3 + H_2O \quad .$$

Chambers and Sherwood[9], Eagleton, Langer and Pigford[13], and Peters and Holman[27] found nitric oxide in the exit gases. Denbigh and Prince[12], Caudle and Denbigh[8], and Simon[32] found no nitric oxide exiting their absorbers. The occurrence of the mist may be explained either by the existence of the gas-phase reaction, or by the heating which

occurs due to reaction at the gas-liquid interface. Wendel and Pigford[36] suggested that local heating at the interface vaporized some water vapor which subsequently condensed in the cooler bulk gas. This does not explain the results of Goyer[17] who studied the formation of the mist in the absence of an aqueous phase. All experimenters except Denbigh and Prince[12], Caudle and Denbigh[8], and Harris[19] observed the mist in their absorbers.

In all studies, the rate of absorption was directly proportional to the concentration of N_2O_4. As shown by the varying conclusions of each study, a gas-phase or liquid-phase reaction in addition to mass transfer at the gas-liquid boundary may limit the rate. The only direct evidence of a vapor-phase reaction is the existence of nitric oxide in the exit gas stream. Unfortunately, on this point there is no agreement. The existence of a stable fog or mist complicates the problem, not only with reference to the occurrence of the vapor-phase reaction, but relative to the dispersion of the droplets into the liquid.

The overall mechanism may be clarified somewhat if the rate of formation of nitric acid from nitrogen dioxide and water vapor can be determined in the gas phase alone. Then, the rate of reaction can be compared with the absorption rate to determine which mechanism is controlling. To accomplish this, the present study was undertaken to determine the rate of reaction of nitrogen dioxide and water vapor in

the gas phase alone.

C. Gas-Phase Reactions of Nitric Acid Vapor

Only a few studies have been made with nitric acid vapor as a primary reactant. Smith[33] studied the reaction of nitric oxide with nitric acid vapor at low pressure. Nitric oxide was added at partial pressures from one to 40 mm Hg, and nitric acid was added at its vapor pressure (50 mm Hg at 25°C) from zero to 30°C. Analyzing for nitrogen dioxide photometrically, Smith reported that the reaction roughly followed the equation,

$$R_{NO_2} = k(NO)(NO_2)(HNO_3) \quad .$$

The value of k was about 2×10^5 liter^2 mole^{-2} sec^{-1} at 25°C. Water vapor increased the rate. Smith attributed the effect of water to heterogeneous reactions in his reactor. The reaction decreased in rate as the temperature increased from zero to 40°C.

Frejacques and Jolibois[15] studied the decomposition of nitric acid vapor at low pressures. They measured the amount of the resulting nitrogen dioxide photometrically, and also measured the changes in total pressure. The decomposition was second order with respect to nitric acid. Frejacques concluded that the decomposition proceeded by the dehydration of two nitric acid molecules,

$$2HNO_3 = N_2O_5 + H_2O \quad .$$

The overall reaction was,

$$2HNO_3 = 2NO_2 + H_2O + 1/2\ O_2 \quad .$$

The experimental rate was given by the expression,

$$R_{HNO_3} = -k(HNO_3)^2 \quad .$$

The value of the second-order rate constant, k, was 8.4 liter $mole^{-1}$ min^{-1} at 265°C.

When nitric oxide was present, the rate of reaction of nitric acid vapor was first order with respect to both nitric oxide and nitric acid. Frejacques suggested that the acid vapor oxidized nitric oxide by the reaction,

$$NO + HNO_3 = NO_2 + HNO_2 \quad .$$

The experimental rate expression was

$$R_{HNO_3} = -k(NO)(HNO_3) \quad .$$

The value of k was 35 liter $mole^{-1}$ min^{-1} at 265°C. They proposed the following scheme for the overall decomposition:

$$2HNO_3 = N_2O_5 + H_2O$$

$$N_2O_5 = NO_2 + NO_3$$

$$NO_2 + NO_3 = NO_2 + NO + O_2$$

$$NO + NO_3 = 2NO_2$$

$$NO + HNO_3 = NO_2 + HNO_2$$

$$2HNO_2 = NO + NO_2 + H_2O \quad .$$

Johnston, et al[21], studied the decomposition of nitric acid vapor from 100° to 400°C. They used a spectrophotometer to detect both nitrogen dioxide (at 210 millimicrons) and nitric acid vapor (at 436 millimicrons). Johnston found that the decomposition was first order with respect to nitric acid, and relatively independent of the concentration of nitric oxide. He suggested that the reaction,

$$HNO_3 = HO\cdot + NO_2 \quad ,$$

was the initial step in the thermal decomposition. Johnston suggested that the data of Frejacques and Jolibois[15] were taken near the low pressure limit for the reaction. He used this to explain their observation that the thermal decomposition was second order with respect to nitric acid.

The decomposition of nitric acid vapor is slow at ordinary temperatures and need not be considered as an influencing factor in the system of interest. The rate of oxidation of nitric oxide by nitric acid vapor, however, is quite fast. The termolecular rate constant is about ten times greater that that for the oxidation of nitric oxide. As the inverse of the reaction of interest, the reaction of nitric oxide with nitric acid must be taken into account as the reaction of nitrogen dioxide and water vapor proceeds.

III. EXPERIMENTAL METHOD

The present study measured the rate of the gas-phase reaction of nitrogen dioxide with water and the rate of this reaction in the presence of oxygen. From these data, a mechanism of reaction was proposed which accounted for the behavior of the rate as the conditions of reaction changed. The rate of reaction was studied at part-per-million concentrations of nitrogen dioxide, and at fractional-percent concentrations of water vapor. Nitrogen was used as a diluent gas. The half life of the reaction was on the order of several hours.

The experiment differed from all other previous studies in that the reactions were homogeneous, involving only a single phase. Other studies of the gas-phase reaction encountered a mist or condensate during the reaction. Wilson and Miles[37] measured the vapor pressure of nitric acid over aqueous nitric acid solutions. At 20°C, the vapor pressure of the 50-percent acid was about 470 ppm. The vapor pressure of water was 1.02 percent. The vapor pressure of the pure acid was much higher, amounting to 51 mm Hg (7.2 percent at one atm) at 20°C. Forsythe and Giauque[14] suggested that the value for the 50-percent acid should be less than 240 ppm. The studies of Goyer[17] involved initially from 800 to 84,000 ppm of nitrogen dioxide and about 0.5 percent water vapor. At these high concentrations, the formation of nitric acid in the liquid phase could not be

avoided.

The present experiment prevented the formation of a mist by keeping the concentration of nitrogen dioxide below 45 ppm, and that of water vapor below 1.2 percent. In this range of concentrations, no two-phase system will form from these two reactants. Experimentally, no mist or condensate was observed in the glass reactor.

The reactants were drawn from high-pressure cylinders and mixed in a constant-volume batch reactor which had a volume of 4.4 liters. Nitrogen was used to raise the total pressure to one atm. Small samples, each with a volume of 0.1 ml, were withdrawn periodically from the reaction mixture. They were injected into a gas chromatograph by means of a gas sampling valve. The reaction mixture was then analyzed for nitric oxide and nitrogen dioxide. The concentration of these two compounds was obtained as a function of time during the reaction.

The initial concentrations of nitrogen dioxide and water vapor were varied to study the initial rate of reaction with respect to each reactant. An activation energy was determined from the temperature dependence of the initial reaction rate.

Parts-per-million concentrations of nitrogen dioxide were allowed to react with concentrations of water vapor which were at least two orders of magnitude higher. As a result, the concentration of water vapor did not change

measurably during the reaction. The total pressure in each experiment was approximately one atmosphere. The reaction temperature was varied from 25^{o} to $50^{o}C$. All reactions took place in the absence of light.

IV. EXPERIMENTAL APPARATUS

A. Reactor Bay

An insulated reactor bay housed a glass reactor, four stainless-steel hold tanks, and the associated plumbing needed to mix the reaction gases. A schematic of this equipment is given in Figure 1. All tubing and tube fittings were made of 316 stainless steel.

The reactor bay was insulated with a two-inch layer of Fiberglas household insulation. The temperature in the bay was regulated by means of three 600-watt heating coils and a small blower. Two of the coils were connected in series with a Variac variable transformer. The other was connected to a specially-built temperature controller which provided proportional temperature regulation (see Figure 2)[31]. The control circuit was a half-wave phase-controlled power regulator using a thermistor as a temperature-sensing probe. Since the temperature-resistance characteristics of thermistors are highly non-linear, the resistance, R_4, and the resistance of the thermistor must be matched for the temperature range in which the device operates. The temperature of the reactor bay was measured with a mercury bulb thermometer which was calibrated from -10^{o} to $50^{o}C$ in divisions of $0.1^{o}C$.

The reactor was a 4.4-liter Pyrex vessel with a surface-to-volume (S/V) ratio of 0.355 cm^{-1}. The reactor had three

outlets. One was connected to a pressure gauge, one to a gas-mixing manifold, and one to the analytical system. The outlet to the analytical apparatus was a 1/16-inch tube which was silver-soldered into a 3/8-inch Swagelock cap. The total length of the sampling capillary was 12 inches. The Swagelock cap fit over the six-mm tubing which made up the reactor outlets. The other connecting tubing was 1/8-inch tubing, the ends of which were silver-soldered to 1/4-inch sleeves. The valves in the mixing manifold were Whitey 1SV4 V-stem valves with 1/4-inch Swagelock tube fittings. No stopcocks were used so that the system could be pressurized.

The four hold tanks, each with a volume of four liters, were located above the reactor. These were connected to the gas-mixing manifold, and to inlet valves which were located outside the reactor bay. These tanks were used to bring the reactant gases to the temperature of the reactor bay before they were mixed. When necessary, the reactor and hold tanks could be evacuated through the manifold.

The pressure in the reactor was measured with a Wallace and Tiernan Model 145 bourdon-type pressure gauge. The gauge was calibrated in divisions of 0.1 inch Hg from zero to 90.00 inches. Pressures could be read within 0.02 inch Hg uncertainty. When the pressure gauge readings were compared with those of a mercury manometer, they were identical within 0.05 inch Hg. Therefore, no separate calibration

of the gauge was made. A mercury manometer was not used in the system because mercury reacts readily with low concentrations of nitrogen dioxide. Because the bourdon tube was made of bronze, great care was exercised to insure that reaction mixtures did not remain in contact with the gauge after mixing. When under vacuum, the pressure in the reactor was measured with a Televac thermocouple-type electronic vacuum gauge. This instrument was calibrated for pressures from one to 5000 microns (0.001 to 5 mm Hg). Typically, the reactor and accompanying apparatus could be evacuated to below ten microns.

B. Reaction Gases

The gases used in the study were stored in high-pressure cylinders. High-purity dry nitrogen, obtained from Linde, was dried before use by passing it through Molecular Sieve 5A. Oxygen, also supplied by Linde, was similarly dried. Dilute mixtures of nitric oxide and nitrogen dioxide in nitrogen were prepared in the laboratory from the pure gases supplied by Matheson. The mixture of nitrogen dioxide was analyzed by the phenol-disulfonic acid procedure (ASTM D-1608-60) using a Beckman DU spectrophotometer[2]. A modification of this procedure, presented in Appendix A, improved the reproducibility of the method. The mixture of nitrogen dioxide in nitrogen contained 186.4 ($\pm$ 1.5) ppm nitrogen dioxide by volume. The mixture of nitric oxide in nitrogen

contained 220 (± 3.5) ppm nitric oxide in nitrogen.

Water was introduced into the reactor by way of wet nitrogen. High-purity nitrogen was forced twice through distilled water in a bubbler. The bubbler was immersed in a water bath which was continuously agitated. The temperature of the bath was maintained at 19.0 (± 0.2) ^{o}C.

C. Analytical Apparatus

A gas chromatograph was used to measure parts-per-million concentrations of nitrogen dioxide and nitric oxide. A schematic diagram of the device is given in Figure 3. The chromatograph consisted of several parts. These included a Carle Model 1404 purged gas-sampling valve, a Loenco 15A column oven, a Loenco electron-capture detector mounted in a separate oven, a Loenco 15B electrometer, a low-power DC power supply, and a Texas Instruments "Servo-riter" strip-chart recorder.

The sampling valve was a sliding-seal valve equipped with two 100-microliter volume loops. The loops could be connected through Whitey OGS2 toggle valves to a vacuum pump, to the reactor, or to a 20-liter stainless-steel standard tank. This vessel was used to store a standard mixture of nitrogen dioxide which was used to calibrate and condition the chromatograph.

The column oven housed a 15-foot column packed with 15-percent SF-96 (by weight) on 40/80 mesh Teflon 6. This column is described below. High-purity, dry nitrogen,

cleaned by passing it through molecular sieves, was used as a carrier gas. A second stream of nitrogen, the scavenger gas, was added to the carrier stream at the exit of the column. This stream lowered the average residence time of the carrier gas in the detector.

A Loenco electron-capture detector was used with the chromatograph. The detector had a plane-parallel design with a 200-millicurie tritium source. The detector was operated with an applied DC potential and with a nitrogen carrier gas. Another common method of operation, using a pulsed DC potential and an argon carrier gas, was found to be less sensitive to nitrogen dioxide and insensitive to nitric oxide. The total nitrogen flow through the detector was large, running about 200 ml min^{-1}. The backround current through the detector was a function of (1) the applied voltage across the detector, (2) the total nitrogen flow, and (3) the temperatures of both the detector and the carrier gas. There was evidence that the backround current was due to impurities in the nitrogen, rather than to the nitrogen itself (see Appendix B).

The electrometer was of conventional design. The maximum sensitivity of the instrument was 9.4×10^{-11} amp mv^{-1} of output signal. Random noise typically amounted to about 5×10^{-12} amp. In the range that the data were obtained, the sensitivity was 1.5×10^{-9} amp mv^{-1}. A low-power DC power supply was built to give the voltage across the detec-

tor. The supply voltage was set at 15.1 volts, the value which gave the maximum response for nitrogen dioxide (see Appendix B). This value was maintained within 0.003 volts with less than 0.02-percent ripple.

A microhygrometer was built to measure ppm concentrations of water vapor in small samples. A complete description of this instrument is given in Appendix C. Its limiting sensitivity was estimated as about 0.1 ppm of water vapor. In actual use, it was limited by the sampling system to concentrations above two ppm. In the present study, the hygrometer was used only to check the efficiency of the bubbler and to check the reproducibility of the water content in reactor samples. On-line analysis of water vapor was not essential since the concentration of water vapor did not change measurably as the reactions proceeded.

D. Chromatography

The chromatographic separation of nitrogen dioxide from nitrogen, oxygen, nitric oxide and water was made on a column packed with 15 percent SF-96 (by weight) on 40/80 mesh Teflon 6. A sample chromatogram is shown in Figure 4. The properties of the column differed considerably from those of conventional columns.

The separation of nitrogen dioxide from air is difficult. Not only is this substance reactive, but it is polar and always in equilibrium with its dimer, N_2O_4. Conventional methods of separating inorganic gases fail. Nitrogen diox-

ide is adsorbed irreversibly on silica gel, and it chemically attacks both molecular sieves and the porous polymer solid supports. Only Morrison[26] has successfully separated nitrogen dioxide by gas-liquid chromatography. He used a 20-foot column packed with 10-percent (by weight) SF-96 on 40/80 mesh Fluoropak 80. The performance of this column was poor by common standards, but it was sufficient to allow the accurate measurement of nitrogen dioxide.

In the present study, several columns were tried. These are listed in Table 1. The column packed with Poropak P gave excellent separation for large amounts of nitrogen dioxide but was attacked so severely that several nitrated organic gases eluted from the column. At lower concentrations, nitrogen dioxide was not eluted from the column. The column packed with 15 percent SF-96 gave the best overall performance of all columns tried. In its preparation, thirty grams of SF-96 (a methyl-silicone oil) were dissolved in about 200 ml of diethyl ether. This mixture was added to 170 grams of 40/80 mesh Teflon 6 which had been sieved from the product obtained from du Pont. The resulting slurry was mixed thoroughly. The mixture was then placed on a steam bath until dry. The resulting material was packed into a single length of 1/8-inch (0.093-inch i.d.) stainless-steel tubing with a length of 15 feet. Glass wool was used to plug the ends. The column was then bent into an eight-inch coil and placed in the chromatograph. Dry nitrogen

was forced through the column at about 50 ml min^{-1} until the smell of ether was gone from the effluent. The nitrogen flow was stopped, and the temperature of the column oven was raised to 200°C. This "no-flow" conditioning continued overnight. The purpose of this step was to allow redistribution of the silicone oil on the solid support. The column was then cooled, and nitrogen forced through it at the rate of 100 ml min^{-1}. Samples of nitrogen dioxide in nitrogen , obtained from the 20-liter standard tank, were injected continuously into the column for several hours until the peak representing nitrogen dioxide appeared. Continued injections increased the sensitivity of the chromatograph until, after about a week, the response to nitrogen dioxide stabilized. Relatively stable calibrations could then be made.

When the column was not used continually, the sensitivity deteriorated, i.e., the height of the peak corresponding to a known concentration of nitrogen dioxide decreased with time. Before each experimental run, at least 40 samples of nitrogen dioxide were injected into the column, restoring its response.

The deterioration of sensitivity may be due to at least two factors. First, initial samples of nitrogen dioxide may be irreversibly adsorbed on active sites on the solid support. If most of these sites were filled, the resolution for nitrogen dioxide would increase since the column would no longer be a sink for nitrogen dioxide. Over long periods of time,

nitrogen dioxide would desorb from the sites and would have to be replaced before a stable calibration could be made.

A second factor in the deterioration of the response may be the absorption of nitrogen into the liquid phase as N_2O_4. It is generally believed that the dimer predominates as the form of nitrogen dioxide in solution. As a pure liquid under pressure, at least 99 percent of the nitrogen dioxide occurs as N_2O_4. In gas-liquid chromatography, the concentration of N_2O_4 in the silicone oil would become more or less stable. The presence of the dimer would influence the reversible absorption-desorption cycle which is characteristic of gas-liquid chromatography. The N_2O_4 would, however, elute from the column over an extended period of time, and would have to be replaced before a stable peak for nitrogen dioxide could be obtained.

The overall deterioration of response as well as the unsymmetrical nature of the response to nitrogen dioxide suggests that the chromatograph was sensitive to both factors. A Teflon column packing was used as a solid support to minimize the activity of the support.

In the operation of the chromatograph, a large number of samples from the standard tank were first injected into the column to achieve a stable response for nitrogen dioxide. Typically, 30 to 50 samples were required. Following this, a single, standard sample was injected five minutes before the reactor was sampled. During this interval, the

reaction gases were mixed. Next, a reactor sample was injected into the column, and an analysis of nitric oxide and nitrogen dioxide was made. Nitric oxide appeared as the first sharp peak. Nitrogen dioxide appeared as a strong, wide, highly unsymmetrical peak with a characteristic tail. It was believed that the tail was due to the equilibrium reaction

$$2NO_2 = N_2O_4 \quad ,$$

which precludes the formation of a Gaussian-appearing peak. Five minutes after the reactor was sampled, another sample was put through the column. The standard sample of nitrogen dioxide gave an internal standard with which to compare the reactor samples. If the calibration for nitrogen dioxide was found to drift, it was corrected by a linear factor obtained from the comparable peak heights of the standard samples. In practice, the response for the standard samples was reproducible within about one percent (one full chart division).

Calibrations were made by measuring the response of the chromatograph to successive dilutions of the standard high-pressure mixture of nitrogen dioxide. It was convenient to fill the reactor initially to a pressure of 30.00 in. Hg with a mixture of nitrogen dioxide in nitrogen, to evacuate to 21.20 in. Hg, and to refill the reactor with dry nitrogen to a pressure of 30.00 in. Hg. By repeatedly evacuating to 21.20 in. Hg and refilling with dry nitrogen, successive

concentrations of nitrogen dioxide differing by the factor, $1/\sqrt{2}$ (= 21.20/30.00), were obtained. Experimenatally, this procedure allowed a quick calibration where the concentration of nitrogen dioxide was halved for every other dilution. A sample calibration is shown in Figure 5.

E. Estimate of Experimental Error

The accuracy of the analysis was good for nitrogen dioxide and poor for nitric oxide. Reproducibility within three percent was obtainable for samples of nitrogen dioxide ranging in concentration from 6×10^{-8} to 2×10^{-6} moles $liter^{-1}$ (1.5 to 40 ppm). At higher concentrations, the response for nitrogen dioxide did not change sufficiently as the concentration of nitrogen dioxide increased. At lower concentrations, the response for nitrogen dioxide became weak, and could not be measured with a precision greater than five percent. The analysis for nitric oxide was less accurate, largely because of the small concentrations involved. The threshhold of response was about 1.5×10^{-8} moles $liter^{-1}$. The increased sensitivity over that for nitrogen dioxide was attributed to the concentration of nitric oxide within the peak rather than to the sensitivity of the electron-capture detector to nitric oxide. Measurements for nitric oxide varied by as much as 20 percent at lower concentrations. At concentrations above about 5×10^{-8} moles $liter^{-1}$, determinations of nitric oxide were reproducible within seven percent. Part of the variation was due

to the speed at which the sampling valve was operated.

Error in mixing was less than 0.1 percent and is not considered important. The concentration of water vapor in the wet nitrogen, however, was always subject to question. Hygrometer measurements showed that reproducible water samples were obtained. Slight fluctuations in the temperature of the water bath surrounding the nitrogen bubbler, however, would appreciably change the concentration of water entering the reactor. The temperature of the bath was maintained closely at 19°C. Nitrogen was forced continously through the bubbler so that the wet nitrogen was constantly replaced (this also removed traces of oxygen). It is believed that the concentration of water in the nitrogen did not change by more than one percent (the variation in vapor pressure of water for a 0.2°C temperature change at 19°C). Overall, the experimental equipment gave excellent results.

V. EXPERIMENTAL PROCEDURE

Before an experimental run was made, the reactor was evacuated to a pressure of less than five microns. It was then pressurized to one atm with dry nitrogen, and again evacuated. This procedure was followed to reduce or eliminate residual water, nitrogen dioxide, or acid vapors from the surface of the reactor. The chromatograph was prepared as discussed before.

The mixture of nitrogen dioxide was added to the evacuated reactor. Wet nitrogen was added next. The timing of the reaction began at the start of this step. Finally, dry nitrogen was added until the total pressure was exactly 30.00 in. Hg (1.003 atm). When oxygen was present, it was added as the second reactant. Then, timing began at the third step when wet nitrogen was added.

Samples were withdrawn at five- or ten-minute intervals, the first sample being withdrawn after about one minute. The reaction was often followed over a period of several days.

Time-concentration profiles for nitrogen dioxide were plotted and smoothed on 50-cm graph paper. The data at 25°C were compared with profiles calculated by computer (see Appendix E) for various systems of equations which were proposed to describe the reaction. When agreement was found, the system of equations were compared with data at higher temperatures with the aid of known thermodynamic quantities.

The thermodynamic values used in the present study are listed in Table 2. Values for the free energy of formation for nitric oxide, nitrogen dioxide, oxygen and water vapor were obtained from Pitzer and Brewer[29]. For nitrous acid vapor, the value was obtained from the data of Ashmore and Tyler on the gas-phase equilibrium of the reaction,

$$NO + NO_2 + H_2O = 2HNO_2 \quad .$$

The free energy of formation of nitric acid vapor was measured directly as part of the present experimental program.

The free energy of formation of each component at temperatures other than 25°C were calculated by the equations,

$$\Delta H_o^o = \Delta F_{25}^o - T\Delta(F_{25}^o - H_o^o)/T$$

$$\Delta F_T^o = \Delta H_o^o + T\Delta(F_T^o - H_o^o)/T \quad ,$$

where the quantity, (F-H)/T, is the free energy function. For nitric acid vapor, the free energy function was obtained from the calculations of Forsythe and Giauque[14]. The values for nitrous acid vapor and for nitrogen dioxide were obtained from the calculations of Altshuller[1]. Other values were obtained from Rossini[30].

VI. EXPERIMENTAL RESULTS

A. Systems Studied

Experimental data were obtained for three reaction systems. The first was the gas-phase reaction of nitrogen dioxide with water vapor. Variables among the various runs were temperature and the concentrations of nitrogen dioxide and water vapor. The reaction was studied at five-degree intervals from 25° to 50°C. The initial concentrations of nitrogen dioxide and water vapor were varied by factors of three and four, respectively, at each temperature. The initial concentration of nitrogen dioxide was varied from 15.5 to 46.5 ppm (6.345×10^{-7} to 1.904×10^{-6} moles liter^{-1} at 25°C). Water was present initially in concentrations from 3.03×10^{3} to 1.21×10^{4} ppm (1.24×10^{-4} to 4.96×10^{-6} moles liter^{-1} at 25°C). The experimental data are presented in Appendix D. A summary of the initial conditions for each test is included.

Other data were obtained for systems involving primarily nitrogen dioxide and water, but with oxygen or nitric oxide added as initial reactants. Three runs with each three-component system were made at 25°C. Oxygen was present in each of the three runs at a concentration of 3.33 percent (1.336×10^{-3} moles liter^{-1} at 25°C). Nitric oxide was present in three runs at a concentration of 520 ppm (2.127×10^{-5} moles liter^{-1} at 25°C). The data for these runs are included in Appendix D.

In the tests in which the reactants were nitrogen dioxide and water vapor only, the concentration of nitrogen dioxide decreased monotonically towards a non-zero equilibrium value. The position of this equilibrium was a strong function of temperature. Figure 6 shows data for three similar runs (runs 5, 21 and 37) which were taken at different temperatures (25^{o}, 35^{o} and 45^{o}C, respectively). Each test began with 31 ppm nitrogen dioxide and 3.03×10^{3} ppm water vapor. The concentrations in each run were slightly different, being in the ratio of their absolute temperatures. The run at 45^{o}C was only 35 percent complete after 2000 minutes. After this time, the runs at 25^{o} and 35^{o}C were 54 and 45 percent complete, respectively. The solid lines in the figure represent the predicted values for nitrogen dioxide, to be discussed later.

The rate of reaction was not dependent on the extent of the reactor surface. Runs with reactors of different surface-to-volume ratios (0.355 cm^{-1} and 1.2 cm^{-1}) but with identical reactant concentrations showed little change in the characteristics of the reaction. The reaction appeared to be a homogeneous gas-phase reaction.

The equilibrium value for nitrogen dioxide was less than predicted for the gas-phase reaction,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad , \qquad (A)$$

when accepted thermodynamic values were used to calculate

the equilibrium constant, K_A. Principally, the value of the free energy of nitric acid vapor reported by Forsythe and Giauque[14] (-17.554 kcal) was open to question.

B. Stoichiometry

The concentrations of both nitric oxide and nitrogen dioxide were monitored as a function of time during the reaction. The concentration of nitric oxide increased in each test from zero as the reaction progressed. According to reaction (A), the stoichiometric relationship between the concentrations of the two oxides should be,

$$(NO) = 1/3\ [(NO_2)_o - (NO_2)] \quad . \qquad (1)$$

This equation is compared to the data for test 17 in Figure 7. The initial concentration of nitrogen dioxide was 15.5 ppm, and that of water vapor was 3.03×10^3 ppm. In each test, the concentration of nitric oxide was less than predicted by equation (1), but not by more than about 15 percent. The agreement was sufficient to confirm that the overall reaction, reaction (A), was occurring.

In each test, a stoichiometric deficiency of nitric oxide relative to nitrogen dioxide was found. The nitric oxide which was not accounted for was believed adsorbed on the surface of the glass reactor. Later studies concerning the oxidation of nitric oxide in the presence of water vapor (see Part II of this thesis) showed that some surface catalysis, apparently due to adsorbed nitric oxide, occurs on

the glass surface. Greig and Hall[38] have reported similar behavior. The discrepancy between the experimental and predicted concentrations of nitric oxide represented small absolute values. For example, in test 17 (Figure 7), the deviation represented about 0.003 mg of nitric oxide adsorbed over 1600 cm^2 of reactor surface. A systematic analytical error may also have been responsible for the discrepancy.

C. Order of the Reaction with Respect to Water

The order of the reaction with respect to water vapor was found by measuring the initial rate of reaction at different initial concentrations of water vapor. The temperature and the concentration of nitrogen dioxide were fixed. The initial rate of reaction was assumed to follow the form,

$$R_{NO_2} = -k(NO_2)^a(H_2O)^b \quad . \qquad (2)$$

The order with respect to water, b, is given by the equation,

$$b = [\log(R_1/R_2)]/[\log(C_1/C_2)] \quad , \qquad (3)$$

where C_1 and C_2 refer to the initial concentrations of water in two different runs. The value of b was 1.00 ($\pm$ 0.03). Three runs at different concentrations of water vapor are compared in Figure 8. For runs 28, 29 and 30, the concentration of nitrogen dioxide was 31 ppm, and the reaction temperature was 40°C. Figure 9 shows the order with respect to water for the eight tests at 25°C. The purity of the order with respect to water vapor supported the contention that the reaction was truly homogeneous.

The order with respect to nitrogen dioxide could not be determined accurately by the above method. The difficulty was due in part to the greater dependence of the reaction rate on the concentration of nitrogen dioxide. Experimentally, the concentration of nitrogen dioxide changed very quickly in the initial stages of reaction, and the chemical equilibrium rapidly became an influencing factor in the reaction. It was not possible to separate the effects of the equilibrium from the initial order with respect to nitrogen dioxide.

D. The Order of Reaction with Respect to Nitrogen Dioxide

The reaction between nitrogen dioxide and water vapor had the following characteristics:

(1) The concentration of nitrogen dioxide decreased monotonically while the concentration of nitric oxide increased from zero.

(2) The initial reaction rate was first order with respect to water vapor.

(3) The initial order of the reaction with respect to nitrogen dioxide was greater than unity.

(4) The extent of the reaction was dependent on temperature, the reaction going further to completion at lower temperatures.

(5) The concentration of nitrogen dioxide fell below the equilibrium value calculated from thermodynamics

for the overall reaction,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (A)$$

To explain the behavior of the reaction, several empirical equations for the disappearance of nitrogen dioxide were compared to the experimental data. For any one test at 25°C, the equation,

$$R_{NO_2} = -k(NO_2)^4(H_2O) \quad , \qquad (4)$$

gave the best agreement with the experimental data. The value of k, however, was not a constant for different values of reactant concentrations. In addition, equation (4) did not describe the equilibrium nature of the reaction, and seemed to have no theoretical basis with regard to an understanding of the mechanism of reaction. The equation,

$$R_{NO_2} = -k(NO_2)^3(H_2O)/(NO) \quad , \qquad (5)$$

gave satisfactory agreement with the experimental data below 40°C, but again, the value of k varied with the concentrations of the reactants.

The empirical rate expression which gave the best agreement for all temperatures and described the equilibrium behavior of the reaction was,

$$R_{NO_2} = -2k_1(NO_2)^2(H_2O) + 2k_2(HNO_2)(HNO_3) \quad , \qquad (6)$$

derived from the proposed overall reaction,

$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad . \qquad (B)$$

The factor of two preceding the rate constants was included because nitrogen dioxide was consumed at twice the rate at which nitric acid was produced. Peters, Ross and Klein[28] also used equation (6) to describe the gas-phase reaction, although they measured no reaction rate. Reaction (B), expressed in the form of the two equations,

$$2NO_2 = N_2O_4 \qquad (C)$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \quad , \qquad (D)$$

is a commonly proposed reaction used to describe the conversion of nitrogen dioxide to nitric acid in aqueous solutions. Time-concentration profiles for nitrogen dioxide were obtained from equation (6) as described in Appendix E. The value of k_1 was 5.50 ($\pm$ 0.29) x 10^4 liter^2 mole^{-2} sec^{-1} at 25°C. The value of k_2 was 5.85 ($\pm$ 0.31) x 10^3 liter mole^{-1} sec^{-1} at 25°C. Values at other temperatures are listed in Table 3. The rate of reaction decreased slightly with temperature. The values of k_1 and k_2 are interdependent, being related by the equilibrium constant for reaction (B) which can be calculated from thermodynamics. Experimentally, the values of k_1 and k_2 did not correspond to the calculated equilibrium values. Therefore, new equilibrium values, presented in the following section, were obtained.

E. The Free Energy of Formation of Nitric Acid Vapor

The values of both k_1 and k_2 in equation (6) were varied to obtain agreement with the experimental points at

25°C. These values cannot be varied independently, however, without changing the thermodynamics of the reaction. At equilibrium, R_{NO_2} reduces to zero, and the forward and reverse rates for reaction (B) are equal:

$$0 = -2k_1(NO_2)^2(H_2O) + 2k_2(HNO_2)(HNO_3) \quad . \quad (7)$$

The constants, k_1 and k_2, are related according to the equations,

$$K_B = k_1/k_2 = (HNO_2)(HNO_3)/(NO_2)^2(H_2O) \quad , \quad (8)$$

and

$$k_2 = K_B k_1 \quad , \quad (9)$$

where K_B is expressed in terms of concentrations. Thus, equation (6) can be expressed in terms of k_1 and K_B:

$$R_{NO_2} = -2k_1(NO_2)^2(H_2O) + 2(k_1/K_B)(HNO_2)(HNO_3) . \quad (10)$$

Since the value of K_B can be calculated from thermodynamics, equation (10) should predict the behavior of reaction (B) when only the value of k_1 is varied arbitrarily. This was found not to be the case. The value of K_B was recalculated from the experimental data at 25°C by the following method.

The equilibrium constant for reaction (B) is related to the change in free energy of the reaction by the equation,

$$K_B = RT \exp(-\Delta F_R/RT) \quad , \quad (11)$$

where K_B is expressed in terms of concentrations. The value of ΔF_R is found by summing the free energies of formation of products and reactants.

$$\Delta F_R = \Delta F_{HNO_2} + \Delta F_{HNO_3} - 2\Delta F_{NO_2} - \Delta F_{H_2O} \quad . \quad (12)$$

The free energies of nitrogen dioxide and water vapor are well-established. The value for nitrous acid vapor was calculated recently by Ashmore and Tyler[3] and by Waldorf and Babb[35], and is believed to be accurate. The value of the free energy for nitric acid vapor is still subject to question. The commonly accepted value of -17.554 kilocalories, calculated by Forsythe and Giauque[14] was determined from incomplete data[39]. With this in mind, the value of the free energy of nitric acid vapor was recalculated from the experimental values of k_1 and k_2 at 25°C by means of equations (9) to (12). It should be noted that the equilibrium constant was calculated by comparison of the values of k_1 and k_2, and not by the experimental determination of the equilibrium concentrations of the products. Their values were not directly obtainable, due both to the slowness with which equilibrium was achieved, and to the lack of an analytical technique for all the products.

The newly calculated value for the free energy of nitric acid vapor was -18.58 ($\pm$ 0.04) kilocalories. By comparison, Forsythe and Giauque[14] reported a value of -17.554 kcal, Lewis and Randall[24] reported a value of -18.21 kcal, and Krase[22] reported a value of -18.56 kcal. The value reported by Forsythe and Giauque was calculated from calorimetric and spectroscopic data. Lewis and Randall, and Krase, calculated the equilibrium constant from vapor

pressure measurements. In the present studies, the equilibrium concentration of nitrogen dioxide fell well below the value predicted by Forsythe and Giauque. It is believed that the present value, and that of Krase, is a more accurate value for the free energy of nitric acid vapor.

Values of the free energy at other temperatures were calculated from the new value at 25°C and the free energy function data of Forsythe and Giauque[14]. For temperatures other than 25°C, the experimental data were fitted to equation (6) by varying only the value of k_1.

F. Mechanism of Reaction

The following reactions are proposed to describe the reaction of nitrogen dioxide with water vapor to form nitric acid vapor:

$$2NO_2 = N_2O_4 \qquad \text{(fast)} \quad \text{(C)}$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad \text{(slow)} \quad \text{(D)}$$

$$2HNO_2 = NO + NO_2 + H_2O \quad . \qquad \text{(fast)} \quad \text{(E)}$$

The balanced, overall reaction is

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad \text{(A)}$$

Reactions (C), (D), and (E) have been proposed previously as the mechanism of absorption of nitrogen dioxide into aqueous solutions[6,8,9,11,12,36]. Reactions (D) and (E) are generally supposed to occur only as liquid-phase reactions. Peters, Ross and Klein[28], and Chambers and

Sherwood[9] suggested that reactions (D) and (E) could also occur in the gas phase. The reaction mechanism represented by reactions (C), (D), and (E) has not previously been supported by direct experimental evidence. Reactions (C) and (D) are equivalent to reaction (B), an overall reaction which was obtained empirically. The rate of disappearance of nitrogen dioxide can be described by the equation,

$$R_{NO_2} = -k_D K_C (NO_2)^2 (H_2O) + k_D' (HNO_2)(HNO_3) \quad , \quad (13)$$

or

$$R_{NO_2} = -k_D K_C (NO_2)^2 (H_2O) + (k_D/K_D)(HNO_2)(HNO_3) . \quad (14)$$

Using the thermodynamic data of Hisatsune[20] to calculate the equilibrium constants for reactions (C) and (D), the value of the second-order rate constant, k_D, was found to be 8.12×10^2 liter mole^{-1} sec^{-1} at 25°C. Values at other temperatures are given in Table 3.

Several factors confirm the mechanism represented by reactions (C), (D) and (E). The first is the agreement of experimental time-concentration profiles with profiles predicted by the mechanism. Appendix E describes the system of equations which were solved to obtain the predicted profiles.

Figures 10 to 14 compare experimental data for runs 1, 9, 17, 25 and 33, taken at 25°, 30°, 35°, 40° and 45°C, respectively. The initial concentration of nitrogen dioxide in each of these runs was 15.5 ppm. Water was present ini-

tially at 3.03×10^3 ppm. The agreement with the predicted values for nitrogen dioxide was best at 25°C, and poorer for the intermediate temperatures. Runs at 45° and 50°C showed better agreement than those at 35° and 40°C. Since the data were fitted primarily at 25°C, the agreement should be very close at this temperature. The other runs were correlated using the data of Forsythe and Giauque. Their data generally predicts a smaller absolute value for the free energy of nitric acid vapor at the intermediate temperatures than was found in the present work, and an increasingly larger value at higher temperatures.

The comparison of the concentration of nitric oxide in Figures 10 to 14 to the predicted profiles are much poorer, due partly both to a poorer chemical analysis, and to the probable adsorption or reaction of nitric oxide on the surface of the reactor. Qualitatively, the profile for nitric oxide is described well by the proposed mechanism.

The second facter which supports the three-step mechanism is the determination that the initial reaction rate is first order with respect to water vapor. This fact limits the possibilities for the rate-controlling step to bimolecular reactions involving water vapor. The other reactant cannot be specified, but conceivably it must be a higher oxide of nitrogen such as N_2O_3, N_2O_4 or N_2O_5. Also, since the reactions took place at relatively high pressure, it can be expected that energy transfer did not limit the rate.

Reaction (C) is often proposed as the initiating reaction for the formation of nitric acid in either phase. The reason is two-fold. First, the equilibrium between nitrogen dioxide and N_2O_4 is known to exist in all phases. The energy of dimerization is very low, probably due to the free-radical nature of nitrogen dioxide attributable to its odd electron. Insertion of reaction (C) into the gas-phase mechanism precludes the necessity to propose a three-body collision in the reaction mechanism. In the present work, it also explains the negative activation energy found experimentally from 25° to $50^{\circ}C$. Nitrogen tetroxide in equilibrium with nitrogen dioxide experiences a rapid decrease in concentration when the temperature of the equilibrium reaction is raised. This is shown in Table 3 by the rapid decrease in the equilibrium constant, K_C. The concentration of N_2O_4 decreases with temperature faster than the second-order rate constant, k_D, increases. Thus the absolute rate of reaction (D) is slower at higher temperatures. This property is expressed in terms of a negative activation energy.

The reaction,

$$2HNO_2 = NO + NO_2 + H_2O \quad , \qquad (E)$$

was studied independently (see Part II of this thesis), and found to be sufficiently fast so as not to influence the rate of reaction. It should be noted that the predicted profiles indicate the presence of less than 0.1 ppm of nitrous acid vapor in the system for all runs.

The reaction,

$$NO_2 + HNO_2 = NO + HNO_3 \quad , \qquad (F)$$

was also found in Part II to be slow relative to reaction (E). This precluded the mechanism,

$$2NO_2 = N_2O_4 \qquad \text{(fast)} \quad (C)$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad \text{(slow)} \quad (D)$$

$$NO_2 + HNO_2 = NO + HNO_3 \ , \qquad \text{(fast)} \quad (F)$$

which would generate the same kinetics as reactions (C), (D) and (E).

G. Activation Energies

The activation energy for the third-order reaction, reaction (B), was calculated from the temperature dependence of the rate constant and the Arrhenius equation,

$$k = k_o \exp(-E_a/RT) \quad . \qquad (15)$$

From the plot shown in Figure 15, an activation energy, E_a, of -978 ($\pm$ 20) calories was found.

The activation energy for reaction (D) was found to be 12.1 ($\pm$ 0.5) kilocalories. An Arrhenius plot for reaction (D) is shown in Figure 16. The frequency factor, k_o, was 6.0×10^{11} liter mole^{-1} sec^{-1}.

H. The Effect of Added Oxygen

The presence of up to three percent oxygen in the system containing initially nitrogen dioxide and water vapor

did not change the initial rate of reaction. For three tests at 25°C, the only change in the overall behavior of the system was the failure of the concentration of nitrogen dioxide to achieve equilibrium (see Figure 17). This was due to the oxidation by oxygen of the resulting nitric oxide according to the reaction,

$$2NO + O_2 = 2NO_2 \quad . \qquad (G)$$

In the presence of oxygen, the reaction mechanism includes the following reactions:

$$2NO_2 = N_2O_4 \qquad \text{(fast)} \quad (C)$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad \text{(slow)} \quad (D)$$

$$2HNO_2 = NO + NO_2 + H_2O \qquad \text{(fast)} \quad (E)$$

$$2NO + O_2 = 2NO_2 \quad . \qquad \text{(slow)} \quad (G)$$

The overall balanced equation is

$$4NO_2 + 2H_2O + O_2 = 4HNO_3 \quad .$$

The overall reaction goes to completion in the gas phase.

The experiments with oxygen demonstrated that nitrous acid vapor was not consumed at an appreciable rate by the overall equation,

$$2HNO_2 + O_2 = 2HNO_3 \quad .$$

Had this reaction occurred at an appreciable rate, the reaction would have followed kinetics described by the equation,

$$R_{NO_2} = -k(NO_2)^2(H_2O) \quad .$$

No equilibrium involving nitrous acid vapor would be established.

I. The Effect of Added Nitric Oxide

The presence of nitric oxide in the system containing nitrogen dioxide and water vapor raised the equilibrium concentration of nitrogen dioxide, and decreased the extent of reaction (see Figure 18). Equilibrium was achieved relatively quickly. The experimental values for nitrogen dioxide were higher than calculated from the mechanism. However, the measured changes in concentration were much lower, e.g., the concentration of nitrogen dioxide in run 51 changed by less than 10 percent during the entire test. Since the errors were larger, accurate interpretation of the data could not be made. Clearly, the overall reaction,

$$NO + 2HNO_3 = 3NO_2 + H_2O \quad ,$$

inhibited the reverse reaction. Nitric oxide is a good reducing agent, and quickly reacts, through the nitrous acid intermediate, with nitric acid vapor.

VII. DISCUSSION OF RESULTS

A. The Gas-Phase Reaction of Nitrogen Dioxide with Water

The gas-phase reaction of nitrogen dioxide with water vapor is a fast, homogeneous reaction that initially follows third-order kinetics according to the equation,

$$R^{o}_{NO_2} = -k(NO_2)^2(H_2O) \quad . \qquad (16)$$

The initial rate of reaction increases as the square of the concentration of nitrogen dioxide. Thus, the reaction can be very slow at low concentrations of nitrogen dioxide, and very fast at higher ones. For a one-percent concentration of water vapor and an initial concentration of ten ppm nitrogen dioxide, the half-life for the reaction, neglecting a back reaction, would be about five hours. If the initial concentration of nitrogen dioxide were increased to 1000 ppm (0.1 percent), the half-life would be about two seconds. The reaction rate increases linearly as the concentration of water vapor increases. The rate is virtually unchanged by the presence of oxygen. Nitric oxide retards the reaction.

The reaction rate is not sensitive to the surface-to-volume ratio of the reactor. Presumably, this shows that the reaction is truly homogeneous. Some absorption of gases did occur in the reactor. A limited amount of water was adsorbed immediately after mixing of reactants. This was demonstrated by measurements with the hygrometer after the reactor was evacuated and quickly refilled with dry nitrogen.

The hygrometer detected water in the bulk gas at concentrations up to 500 ppm. It appeared that nitrogen dioxide and N_2O_4 were not appreciably adsorbed. The concentration of nitrogen dioxide could be followed rather accurately at low concentrations. Amounts as small as 0.01 mg distributed throughout the 4.4-liter reactor would have been detected by difference. No such adsorption was found.

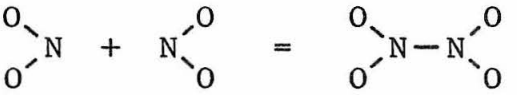
It also seemed likely that, at room temperature, a glass surface would adsorb some nitric acid vapor. According to the present study, adsorption of nitric acid vapor would not change the initial rate, but would tend to lower the value of the free energy of formation of nitric acid vapor calculated from the experimental data. The insensitivity of the reaction to the surface-to-volume ratio of the reactor is primary evidence that nitric acid vapor is not adsorbed. In addition, experimental data were correlated from 25° to 50°C by determining the free energy of formation of nitric acid vapor only at 25°C. Then, using this as a base value, the free energy of the acid vapor and the equilibrium constant for reaction (B) at other temperatures were calculated. At 25°C, adsorption of nitric acid vapor would be the greatest, and error in the correlation would be greatest. It would be coincidence if the temperature dependence of the adsorption matched the correlation.

Adsorption of nitric oxide occurred to a limited extent as shown by the stoichiometric deficiency of nitric oxide

relative to nitrogen dioxide. Interactions of nitric oxide and water on glass surfaces have been discussed by Greig and Hall[38] who reported that nitric oxide catalyzes reactions with nitrogen dioxide on glass surfaces. These effects occurred at 20°C. Other studies, principally those concerned with the air oxidation of nitric oxide, have shown that the dry oxidation is unaffected by reactor surface[26]. In the present experiments, the concentration of nitric oxide could not be measured in concentrations below about 0.5 ppm. As a result, no conclusions can be made as to the influence of the glass surfaces at the beginning of the reaction where the concentration of nitric oxide is quite small. As the concentration of nitric oxide increased, its stoichiometric deficiency decreased, indicating that adsorption of nitric oxide was limited. The adsorption would tend to decrease (make more negative) the value calculated for the free energy of nitric acid vapor. The influence would be small since the equilibrium constant from which the free energy was measured varies as the first power of nitric oxide. In contrast, it varies as the square of the concentration of nitric acid, and as the cube of nitrogen dioxide. In test 1, the deficiency between the predicted and experimental values for nitric oxide leads to a 20 calorie difference in the value of the free energy. This is below the probable error based on the scatter of the data.

B. Mechanism of Reaction

The reaction of nitrogen dioxide with water vapor involves major structural changes in the molecules involved. Dinitrogen tetroxide is a simple association product of two nitrogen dioxide molecules, each with an odd electron,

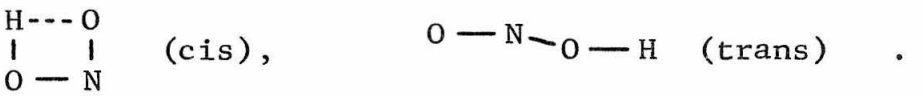


This reaction is very fast, a characteristic often associated with a low (or zero) activation energy such as found in free radical reactions.

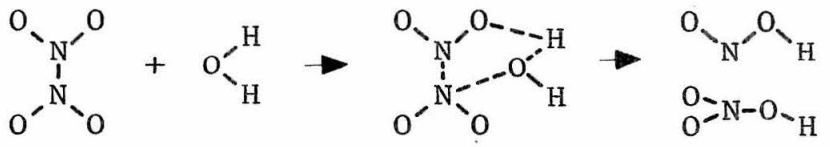
The rate-controlling reaction,

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \quad , \qquad (D)$$

produces nitrous acid vapor, a substance which may occur in two isomeric forms, cis and trans[40]:



It is believed that the rate-controlling reaction may be described by the stereochemical representation,



Thus, nitrous acid would be expected to be the trans isomer. A similar analysis can be made for the reaction

$$2HNO_2 = NO + NO_2 + H_2O \quad .$$

This is included in Section VI of Part II of this thesis. The analysis shows that one molecule each of the cis and trans isomers are involved in the reaction.

As noted before, the proposed mechanism for the reaction of nitrogen dioxide with water vapor,

$$2NO_2 = N_2O_4 \qquad (C)$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad (D)$$

$$2HNO_2 = NO + NO_2 + H_2O \quad , \qquad (E)$$

has been mentioned frequently in the literature as the path to form nitric acid from nitrogen dioxide, especially in the liquid phase. Other mechanisms have been suggested for the gas-phase reaction including those which propose the anhydride of nitric acid, N_2O_5, as the reactive intermediate. Harris[19] suggested that the formation of nitric acid from wet nitrous gases proceeded by the path,

$$NO + O_2 = NO_3 \qquad \text{(fast)} \quad (a)$$

$$NO_2 + NO_3 = N_2O_5 \qquad \text{(fast)} \quad (b)$$

$$N_2O_5 + H_2O = 2HNO_3 \quad . \qquad \text{(slow)} \quad (c)$$

According to this mechanism, the initial reaction rate would be,

$$R_{HNO_3} = k_c K_b K_a (NO)(NO_2)(O_2)(H_2O) \quad .$$

If reaction (b) were rate-controlling, the initial rate would be,

$$R_{HNO_3} = k_b K_a (NO)(NO_2)(O_2) \quad .$$

In both cases, the initial rate would be autocatalytic, would require the presence of oxygen, and would be greatly increased by the presence of oxygen. The present data demonstrated that the initial rate is insensitive to the concentration of oxygen.

Christini[10] suggested that the vapor-phase reaction followed the following reaction path:

$$2NO_2 = N_2O_4 \qquad \text{(fast)(d)}$$

$$N_2O_4 = NO + NO_3 \qquad \text{(fast)(e)}$$

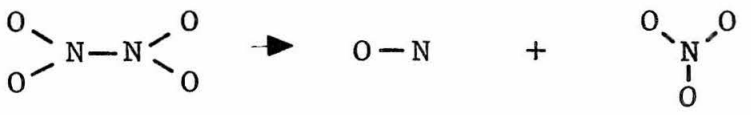
$$NO_2 + NO_3 = N_2O_5 \qquad \text{(fast)(f)}$$

$$N_2O_5 + H_2O = 2HNO_3 \quad . \qquad \text{(slow)(g)}$$

This scheme results in a first-order dependence on water, required by the present data, only if reaction (g) is rate-controlling. The rate of formation of nitric acid according to Christini's path would then be,

$$R_{HNO_3} = k_g K_d K_e K_f (NO_2)^3 (H_2O)/(NO) \quad ,$$

which predicts a higher-order dependence on nitrogen dioxide than was observed in the present work. The equation does describe qualitatively the behavior of the initial rate towards added nitric oxide. It should be noted that reaction (e) is unlikely because it requires major structural changes in the molecules:



Benson[4] has discussed the occurrence of the nitrate radical, NO_3, and suggests that it may occur only in very high energy systems.

The present studies show that the reaction of nitric acid vapor with nitric oxide occurs by the reactions,

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (H)$$

$$HNO_2 + HNO_3 = N_2O_4 + H_2O \qquad (I)$$

$$N_2O_4 = 2NO_2 \quad . \qquad (J)$$

The initial rate of reaction of nitric acid vapor would be,

$$R^o_{HNO_3} = -k_I(HNO_2)(HNO_3) \qquad (17)$$

or

$$R^o_{HNO_3} = -k_I K_H^{\frac{1}{2}}[(NO)(NO_2)(H_2O)]^{\frac{1}{2}}(HNO_3). \qquad (18)$$

Thus, autocatalytic behavior for both nitrogen dioxide and water vapor would be expected. Smith[33] observed such behavior, but attributed the effect due to water on surface reactions. He proposed the equation,

$$R^o_{NO_2} = k(NO)(NO_2)(HNO_3) \quad ,$$

to describe the rate of reaction of nitric oxide with nitric acid vapor although no mechanism was suggested. Johnston[21] found that the low-pressure decomposition of nitric acid vapor was unaffected by the presence of nitric oxide. Since the gas-phase reaction between the two reactants is known to occur, Johnston's work suggests that other substances are required to initiate the reaction.

C. The Absorption of Nitrogen Dioxide into Aqueous Solution

The mechanism of the absorption of nitrogen dioxide into aqueous solutions is complex, probably including to some extent both diffusion-limited and reaction-limited components. The problem is further complicated by occurrence of a mist which arises from the gas-phase reaction when the partial pressure of nitric acid exceeds its vapor pressure. The rate of absorption can, in principle, be controlled by

(1) The rate of the gas-phase reaction

(2) The rate of diffusion of gases in and out of the gas-liquid interface.

(3) The rate of chemical reaction at the gas-liquid interface.

(4) The rate of diffusion of components in and out of the liquid film.

Also to be noted is the rate of mass transfer of nitric acid droplets from the gas to the solution.

At concentrations of nitrogen dioxide on the order of a few percent, experimental data conflict on the mechanism of absorption. Peters, Ross and Klein[28] suggested that the rate of absorption is controlled by the rate of the gas-phase reaction. Chambers and Sherwood[9] and Bolshakoff[5] contend that the rate is controlled by diffusion of gases through the gas film, the principal diffusant being nitrogen dioxide. Caudle and Denbigh[8], Wendel and

Pigford[36], and Carberry[6] suggest that the rate of absorption is controlled by chemical reaction in the liquid.

The present study has shown that, at moderate concentrations of nitrogen dioxide, nitric acid is formed as a vapor quite rapidly. The thermodynamic equilibrium is unfavorable, so that the concentration of nitric acid vapor is limited. Calculations were made under the assumption that the rate of absorption in a wetted-wall column (such as used by Caudle and Denbigh, Chambers and Sherwood, and Wendel and Pigford) was gas-film resistance limited, the primary diffusant being nitric acid vapor. The results match within reasonable error the experimental values of of both Chambers and Sherwood[9] and Wendel and Pigford[36] on the rate of production of nitric acid in solution. This suggests only that nitric acid vapor must be considered as important a gas-phase diffusant as nitrogen dioxide, N_2O_4 or water vapor. The implication is that the overall absorption of nitrogen dioxide at concentrations of a few percent is controlled by resistance to mass transfer in the gas film rather than by the rate of reaction in the liquid phase.

As the concentration of nitrogen dioxide decreases, the importance of the gas-phase reaction and of gas-phase diffusion decreases, and that of liquid-phase reactions increases. The gas-phase reaction becomes slow and occurs to a lesser extent. Reaction of nitrogen dioxide or N_2O_4

with the solution becomes the rate-limiting factor. Only in the liquid is the concentration of water high and the equilibrium favorable. Such is the case in the absorption of oxides of nitrogen from flue gases where the concentration of the total oxides may range roughly from 100 to 2000 ppm. To increase the rate of removal of nitrogen dioxide from the gases, one could add caustic soda to the absorbing solution to speed chemical reaction. For concentrations of nitrogen dioxide above, say, 0.1 percent, this procedure would not speed absorption because the rate of absorption would be relatively independent of the rate of reaction in aqueous solution.

VIII. SUMMARY OF RESULTS

The gas-phase reaction of nitrogen dioxide with water vapor was studied at atmospheric pressure and ambient temperature. Parts-per-million concentrations of nitrogen dioxide reacted with concentrations of water vapor up to 1.2 percent. The overall reaction was,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (A)$$

The initial rate of reaction, determined by following the concentrations of nitric oxide and nitrogen dioxide, was first-order with respect to water vapor, and second-order with respect to nitrogen dioxide. The overall rate followed the semi-empirical equation,

$$R_{NO_2} = -2k_1(NO_2)^2(H_2O) + 2k_2(HNO_2)(HNO_3) \quad . \qquad (6)$$

The value of k_1 was 5.50 ($\pm$ 0.29) x 10^4 liter^2 mole^{-2} sec^{-1} while that of k_2 was 5.85 ($\pm$ 0.31) x 10^3 liter mole^{-1} sec^{-1} at 25°C. Equation (6) describes the rate of the overall reaction,

$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad . \qquad (B)$$

The activation energy for reaction (B) was -978 ($\pm$ 20) calories between 25° and 50°C.

Experimental time-concentration profiles for nitric oxide and nitrogen dioxide were described accurately by the reaction mechanism,

$$2NO_2 = N_2O_4 \qquad \text{(fast)} \quad \text{(C)}$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad \text{(slow)} \quad \text{(D)}$$

$$2HNO_2 = NO + NO_2 + H_2O \quad . \qquad \text{(fast)} \quad \text{(E)}$$

Reaction (D) controlled the rate of reaction. The value of the second-order forward rate constant, k_D, was 8.12×10^2 liter $mole^{-1}$ sec^{-1} at 25°C. The activation energy for reaction (D) was 12.1 ($\pm$ 0.5) kilocalories between 25° and 50°C.

Oxygen did not change the initial rate of reaction, and changed the overall rate only to the extent that it oxidized the resulting nitric oxide. The presence of nitric oxide inhibited the reaction, raising the equilibrium concentration of nitrogen dioxide. Changes in the surface-to-volume ratio of the reactor did not affect the time-concentration profiles for nitrogen dioxide. There was no evidence of adsorption of nitrogen dioxide or of N_2O_4, but appreciable amounts of water vapor and a small amount of nitric oxide was adsorbed.

The free energy of nitric acid vapor was calculated from the equilibrium constant for reaction (B). The latter value was measured from the rate constants as the reaction approached equilibrium at 25°C. The value of the free energy of nitric acid vapor at 25°C was -18.58 ($\pm$ 0.04) kilocalories. This value was in good agreement with other directly-measured values, but in poorer agreement with values calculated from calorimetric and spectroscopic data. The latter values

predicted that the gas-phase reaction would occur to a lesser extent than found in the present studies.

IX. RECOMMENDATIONS

The present study measured the rate of reaction between nitrogen dioxide and water vapor in the gas phase. Experimental data showed that the reaction occurred at a significant rate, and is a factor in the absorption of nitrogen dioxide into aqueous solution. With these data, and knowing the gas-phase diffusion coefficients for nitric oxide, nitrogen dioxide, water vapor, and nitric acid vapor, it should be possible to measure directly the rate of the liquid-phase reaction,

$$3NO_2(g) + H_2O(aq) = NO(g) + 2HNO_3(aq) \quad .$$

Nitrogen dioxide must, however, remain at concentrations below about 50 ppm to prevent the spontaneous formation of a mist. Droplets of nitric acid doubtless have confused much of the work done on the rate of absorption of nitrogen dioxide so far. For analysis, the concentration of nitrogen dioxide in the gas phase could be monitored by gas chromatography, while the concentration of nitric acid in solution could be measured by infrared spectroscopy. Such a study would do much to enable the prediction of absorption rates of nitrogen dioxide from gases.

It would be interesting to measure the effect of addition of hydrogen peroxide to nitric acid solutions, and to aqueous solutions used to absorb nitrogen dioxide. Hydrogen peroxide will stabilize nitric acid with respect to

decomposition according to the overall reaction,

$$2NO_2 + H_2O_2 = 2HNO_3 \quad .$$

In addition, it may increase the rate of absorption of nitrogen dioxide by accelerating the gas-phase reaction. The primary cost of manufacture of nitric acid is in the operation of large absorption towers. It may be economical to add hydrogen peroxide, generated by the 2-ethyl-anthraquinone process, to the final absorption tower to help remove low concentrations of nitric oxide and nitrogen dioxide. Increasing emphasis of controlling emissions from nitric acid plants as well as the possibility of using smaller absorption equipment, may make the use of hydrogen peroxide in nitric acid manufacture economically feasible.

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XI. NOMENCLATURE

Symbols

a	: order of reaction with respect to nitrogen dioxide
b	: order of reaction with respect to water vapor
C	: concentration, moles per liter
E_a	: activation energy, cal/g-mole
ΔF^o	: standard free energy change, cal/g-mole
ΔH_o^o	: standard enthalpy of formation at zero temperature
k	: forward rate constant, appropriate units
k'	: reverse rate constant, appropriate units
k_o	: frequency factor from the Arrhenius equation
k_1	: forward rate constant, defined by equation (6)
k_2	: reverse rate constant, defined by equation (6)
K	: equilibrium constant, expressed in terms of concentrations
R	: rate of reaction, expressed as the rate of production of the subscripted component
S/V	: surface-to-volume ratio, cm^{-1}
t	: time, sec
T	: temperature, ^oK
( )	: concentration, moles $liter^{-1}$

LIST OF TABLES

Table 1. Summary of Chromatographic Studies

Column	Length	Temp	Comments
80/100 Porapak P	10 ft	25-100°C	Separated nitrogen dioxide from air, but was attacked severely.
80/100 Porapak Q,R,S	10 ft	25-100°C	No separation for nitrogen dioxide. All were severely attacked.
80/100 Porapak T	30 ft	25°C	Separated nitrogen, oxygen and nitric oxide. Did not separate nitrogen dioxide.
60/80 Molecular Sieve 13X	10 ft	25-100°C	Gave a poor separation of nitric oxide from air, but resolved nitrogen and oxygen as expected.
10% SE-30 on 40/80 Teflon 6	10 ft	25°C	No separation was found.
80/100 Porapak Q	10 ft	-78°C	Best separation for nitric oxide, nitrogen and oxygen.
		25°C	Excellent separation for CO_2, N_2O
		150°C	Best temperature for the separation of water from air.
10% SF-96 on 80/100 Kel F	10 ft	25°C	No separation of the oxides of nitrogen.
15% SF-96 on 40/80 Fluoropak 80	15 ft	25°C	A poor separation for nitrogen dioxide. Morrison's results were not duplicated.
15% SF-96 on 60/80 HMDS Chromosorb W	30 ft	25-50°C	Long column gave the best resolution for nitrogen dioxide, but gave the poorest efficiency.
15% SF-96 on 40/80 Teflon 6	15 ft	25°C	Gave the most satisfactory separation of nitrogen dioxide from air.

Table 2. Summary of Thermodynamic Data

	Temp	Free Energy Function	Heat Content Function	Free Energy @ 25°C	Ref
	(°K)	(cal/°K)	(cal/°K)	(cal)	
NO	300	-41.667	7.411	20,723	29,30
	325	-43.028	7.356		
NO_2	300	-49.190	8.180	12,341	29,30
	325	-49.850	8.240		
NO_3	300	-51.620	8.800	27,360	20
	325	-52.340	9.010		
N_2O_3	300	-62.030	11.980	33,490	20
	325	-63.000	12.290		
N_2O_4	300	-59.660	13.180	23,660	20
	325	-61.400	13.620		
N_2O_5	300	-70.870	14.250	28,180	20
	325	-72.040	14.750		
H_2O	300	-37.214	7.940	-54,638	29,30
	325	-39.505	7.985		
HNO_2	300	-52.050	8.890	-10,810	1,3
	325	-52.820	9.070		
HNO_3	300	-54.050	9.390	-18,580	14
	325	-55.050	9.620		

Table 3. Summary of Calculated and Experimental Results

$$2NO_2 + H_2O = HNO_2 + HNO_3 \qquad (B)$$

$$2NO_2 = N_2O_4 \qquad (C)$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \qquad (D)$$

Temperature (°C)	k_B (*)	K_B (**)	k_B' (***)	K_C (**)	k_D (**)
25	5.50×10^4	9.40	5.85×10^3	134.4	8.12×10^2
30	5.21×10^4	7.35	7.09×10^3	95.7	1.10×10^3
35	5.13×10^4	5.78	8.87×10^3	67.7	1.51×10^3
40	4.94×10^4	4.56	1.08×10^4	48.5	2.02×10^3
45	4.81×10^4	3.62	1.33×10^4	35.0	2.75×10^3
50	4.72×10^4	2.92	1.62×10^4	25.4	3.71×10^3

(*): units of $\text{moles}^2\ \text{liter}^{-2}\ \text{sec}^{-1}$

(**): units of liter mole^{-1}

(***): units of $\text{moles liter}^{-1}\ \text{sec}^{-1}$

LIST OF FIGURES

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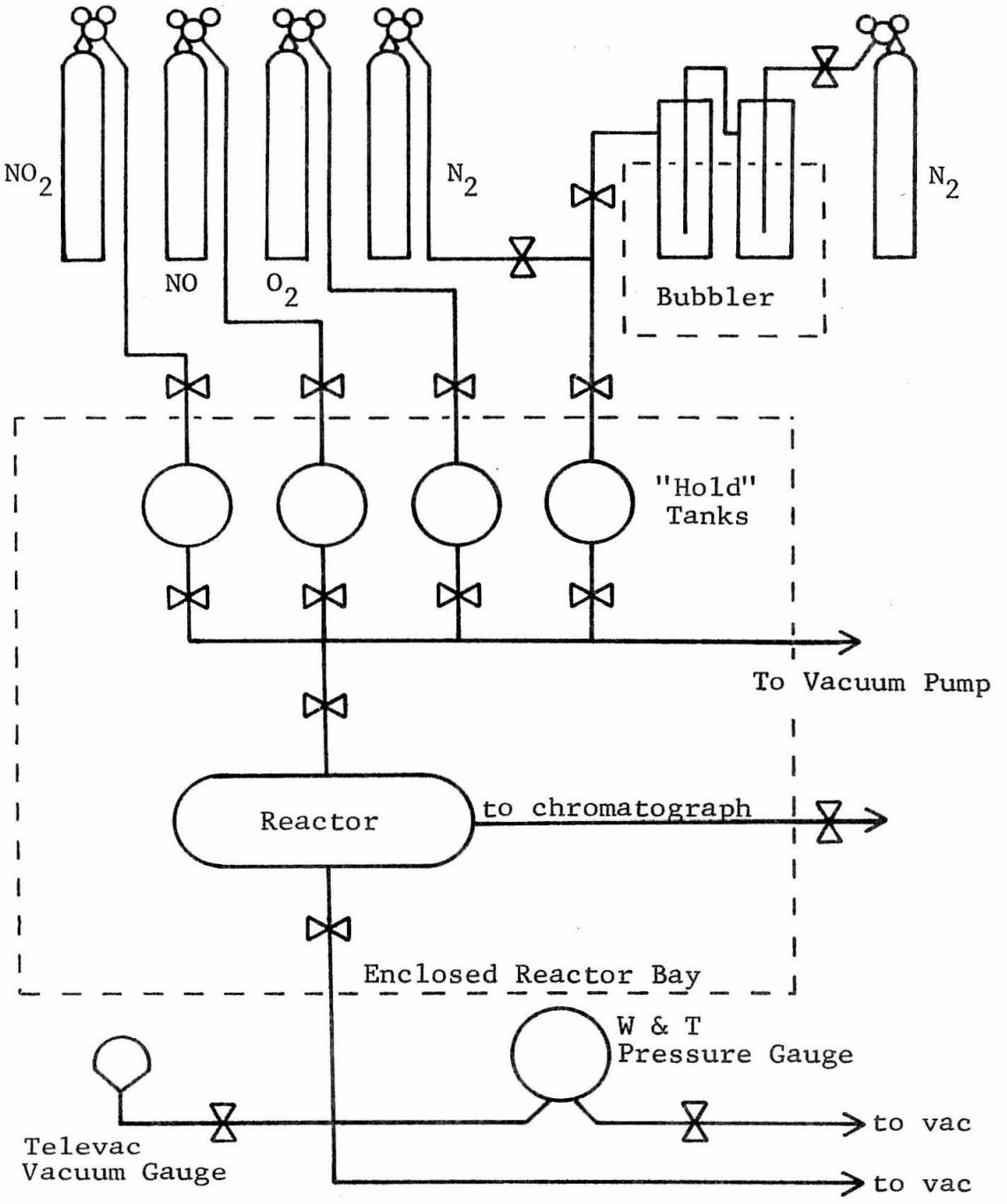


Figure 1. Schematic of the Reactor Bay and Gas-Mixing Apparatus

Parts List

C_1: 0.1 uf, 100-volt capacitor
D_1, D_2, D_3: 1N4004 silicon rectifier, 1 amp, 400 PIV
D_4: 1N1776 Zener diode (two in series), 20-volt, 1-watt
Q_1: 2N2626 unijunction transistor
Q_2: C20B silicon-controlled rectifier, 7.4 amp, 200 PIV
R_1: 2700-ohm, 1-watt resistor
R_2: 5-megohm potentiometer
R_3: 2700-ohm, 1-watt resistor
R_4: 100K, ½-watt resistor
R_5: 10K, ½-watt resistor
R_6: Fenwal LN483 thermistor (100K ohms at 25°C)
R_7: 100-ohm, ½-watt resistor
R_8: 100-ohm, ½-watt resistor
S_1: DPST 15-amp switch

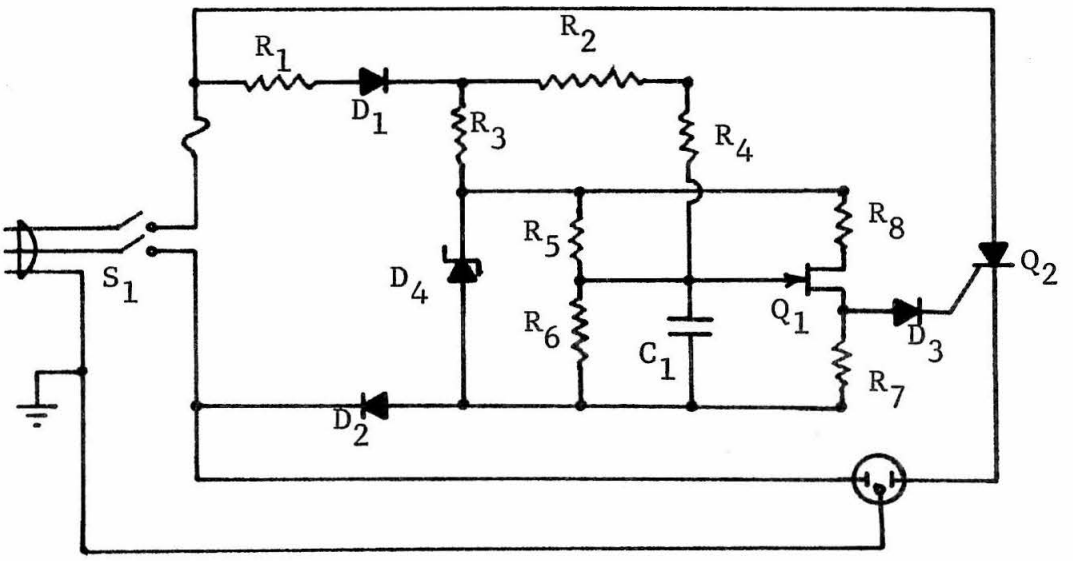


Figure 2. Schematic of Temperature Controller

(see Reference 18)

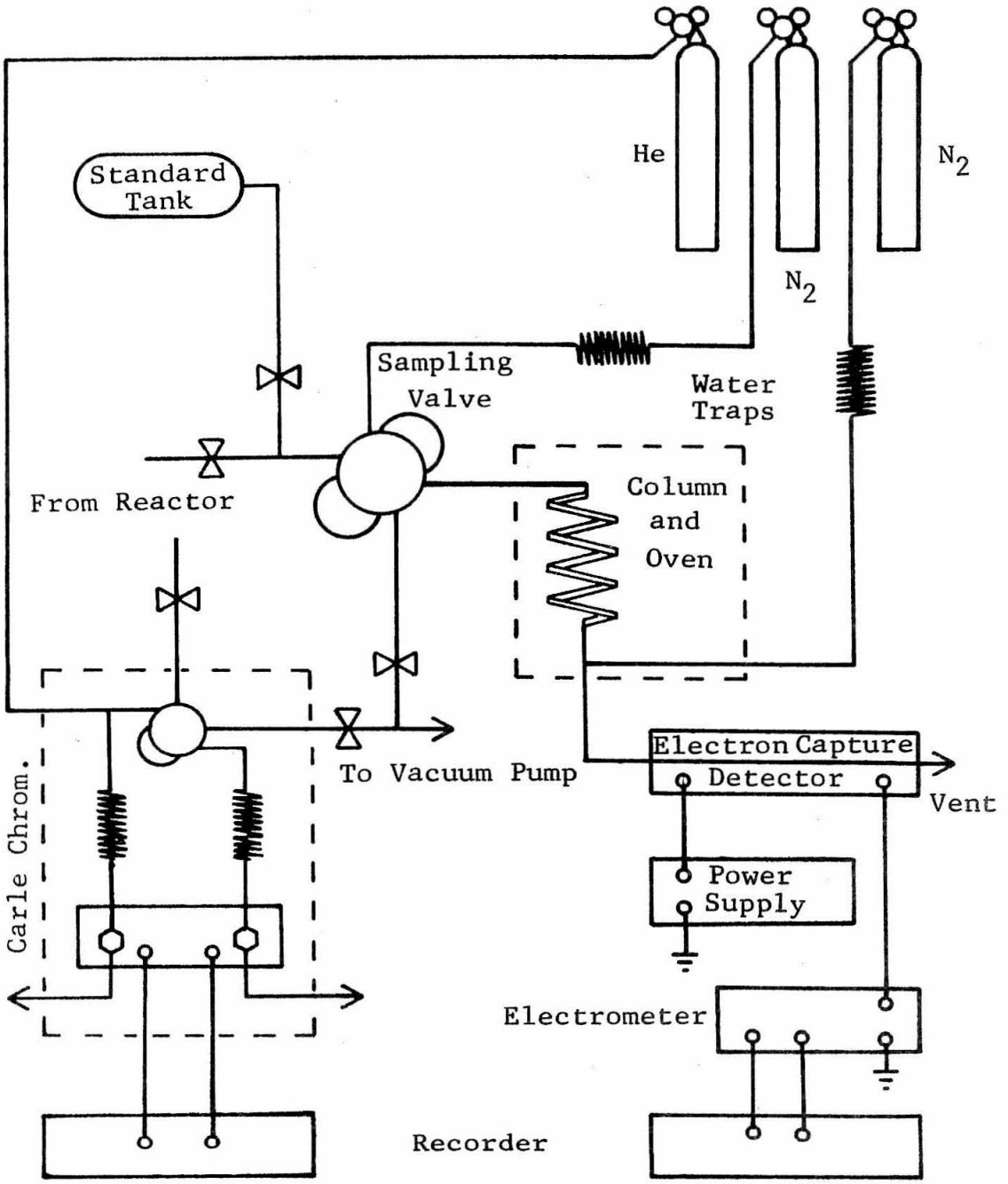


Figure 3. Schematic of Analytical Apparatus

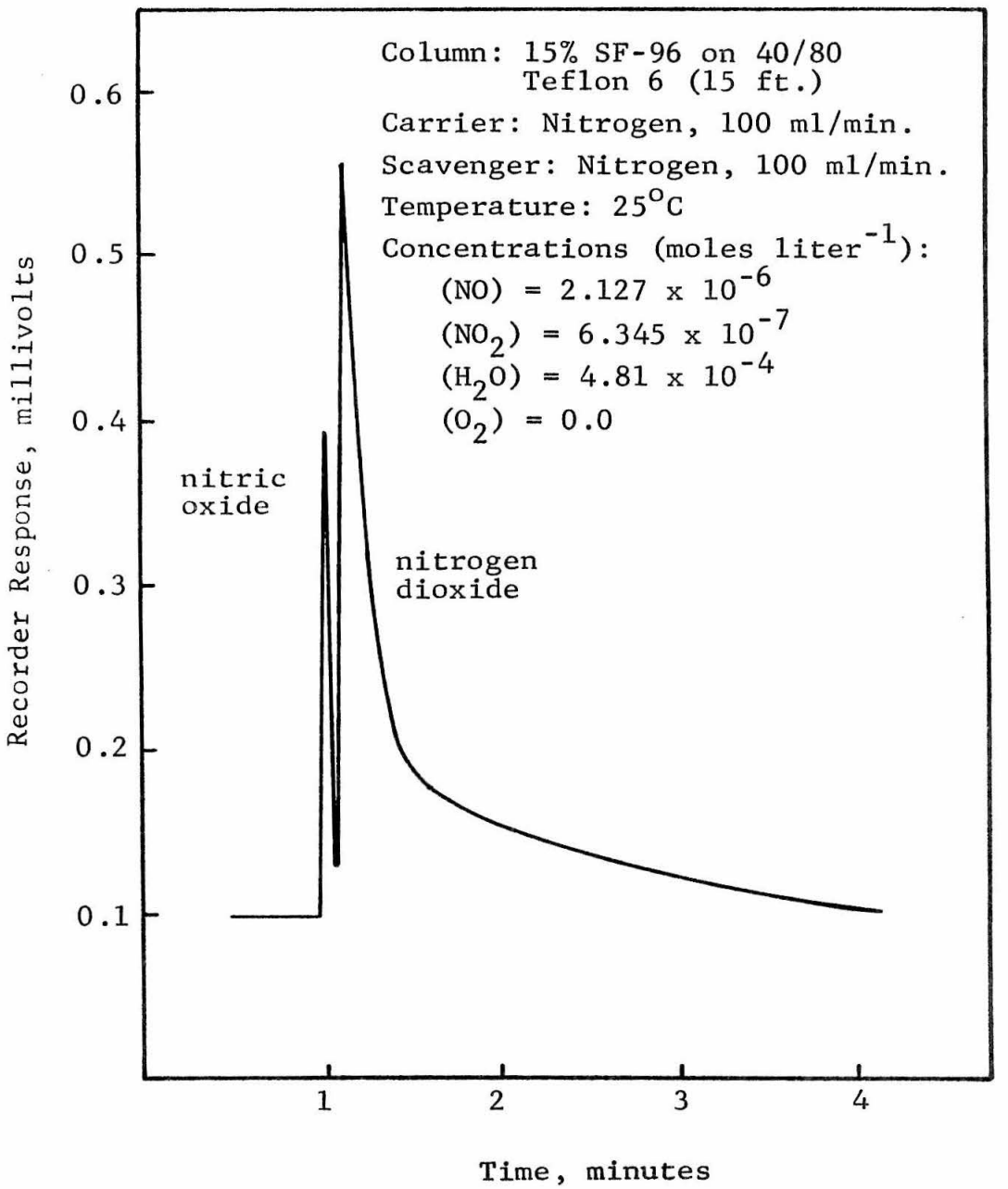


Figure 4. Chromatogram of the Separation of Nitric Oxide from Nitrogen Dioxide in a Wet Nitrogen Environment.

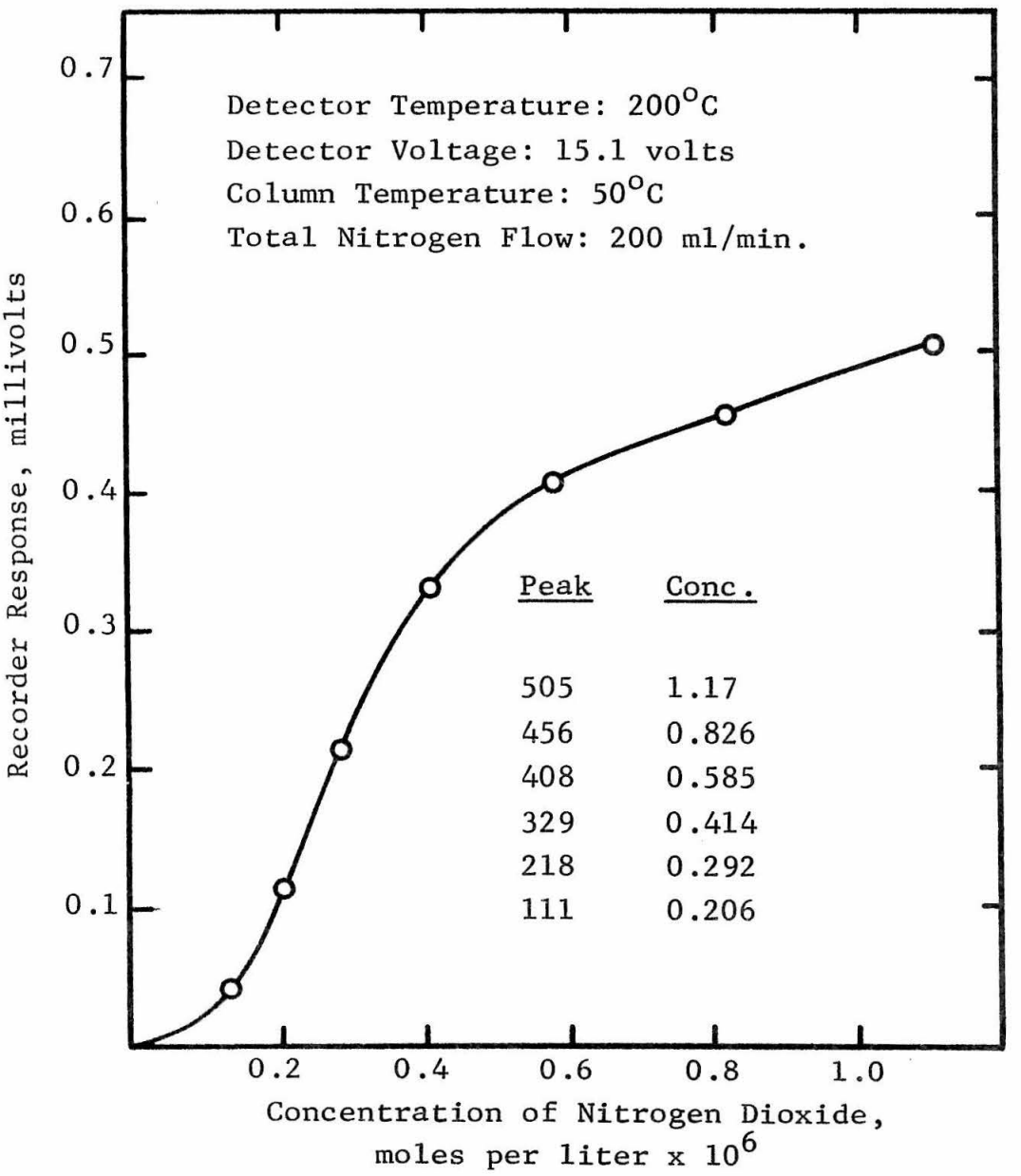


Figure 5. Sample Calibration of the Gas Chromatograph for Nitrogen Dioxide.

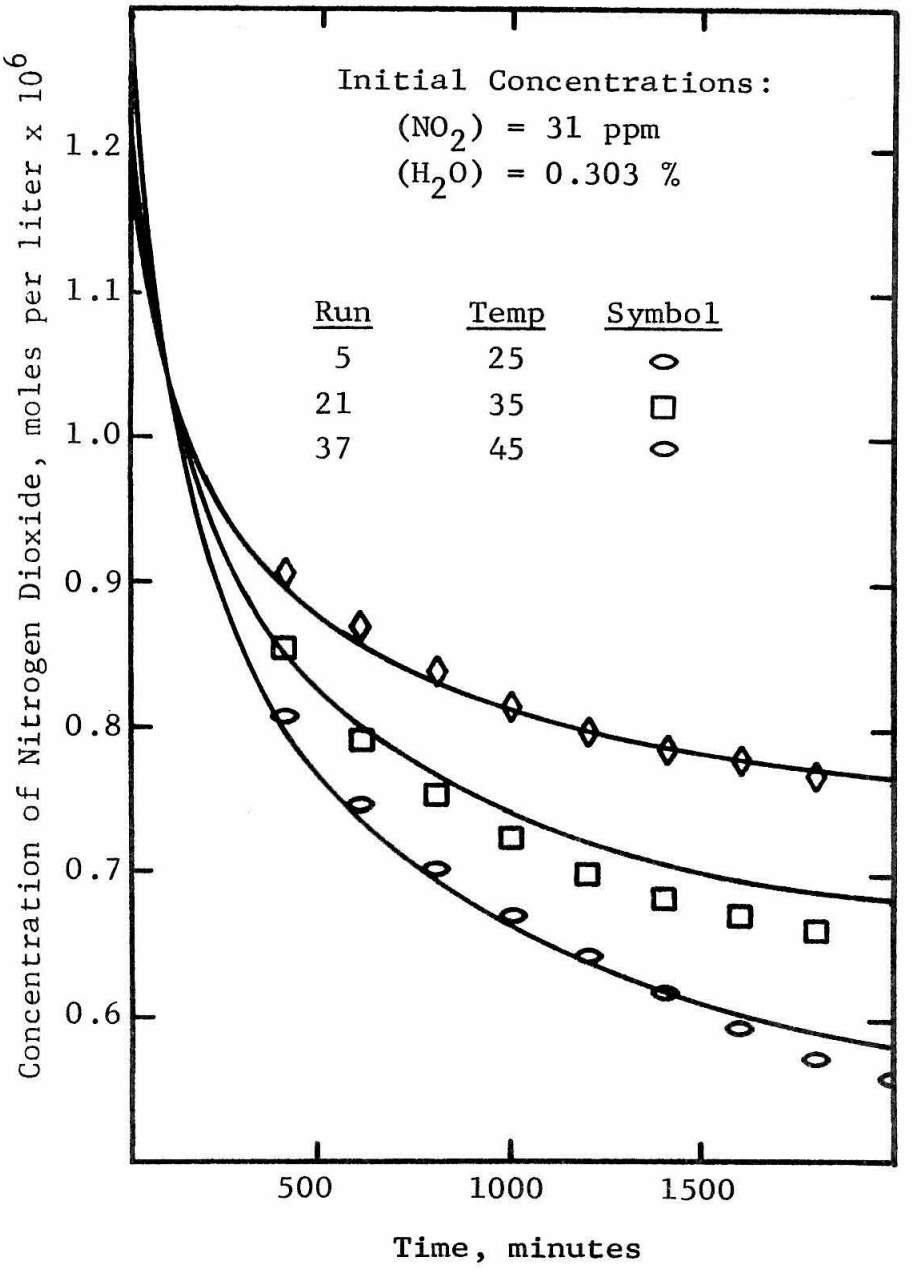


Figure 6. Dependence on Temperature of the Reaction of Nitrogen Dioxide with Water Vapor.

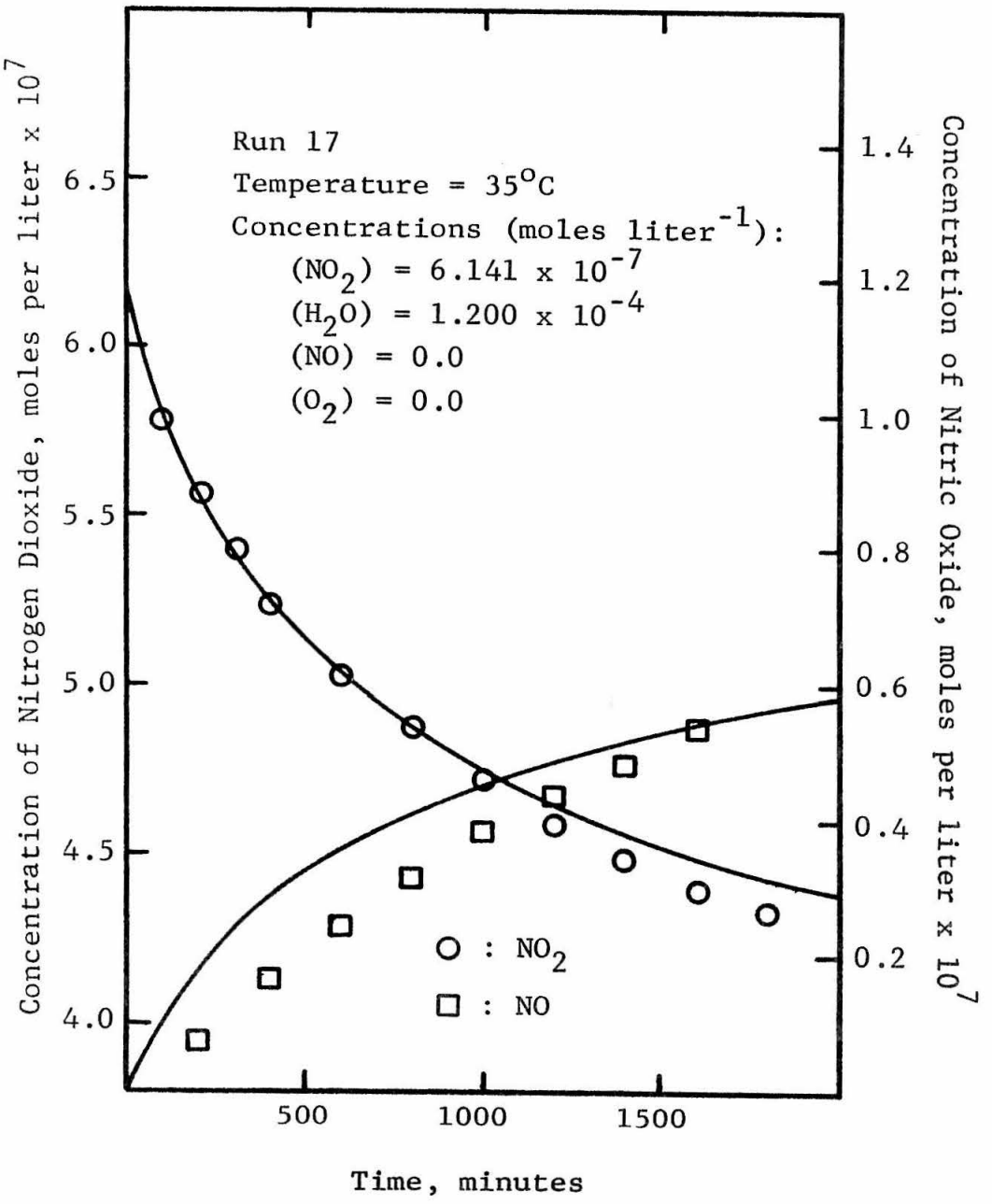


Figure 7. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 17 at 35°C.

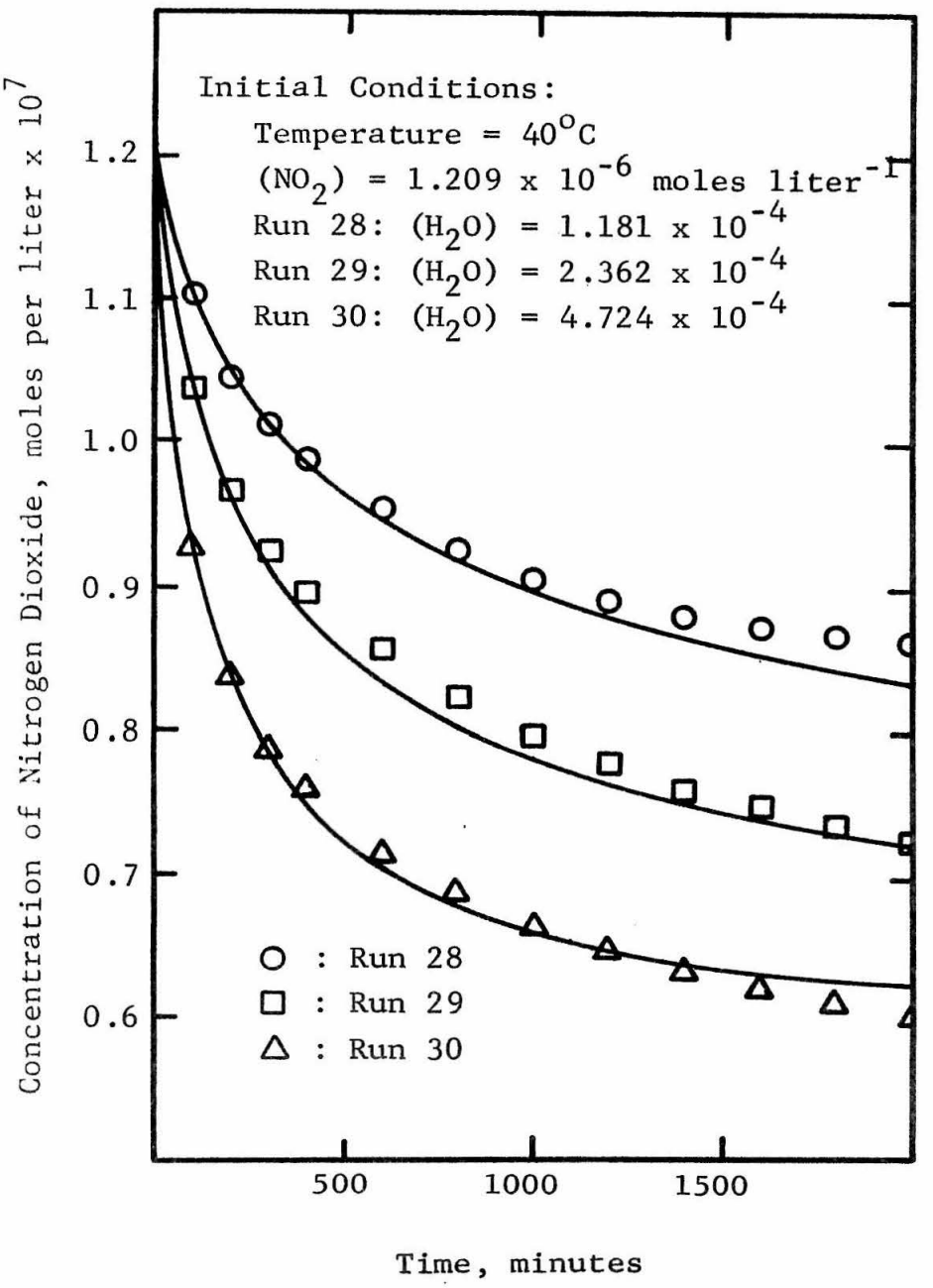


Figure 8. Dependence on Water of the Reaction of Nitrogen Dioxide with Water Vapor.

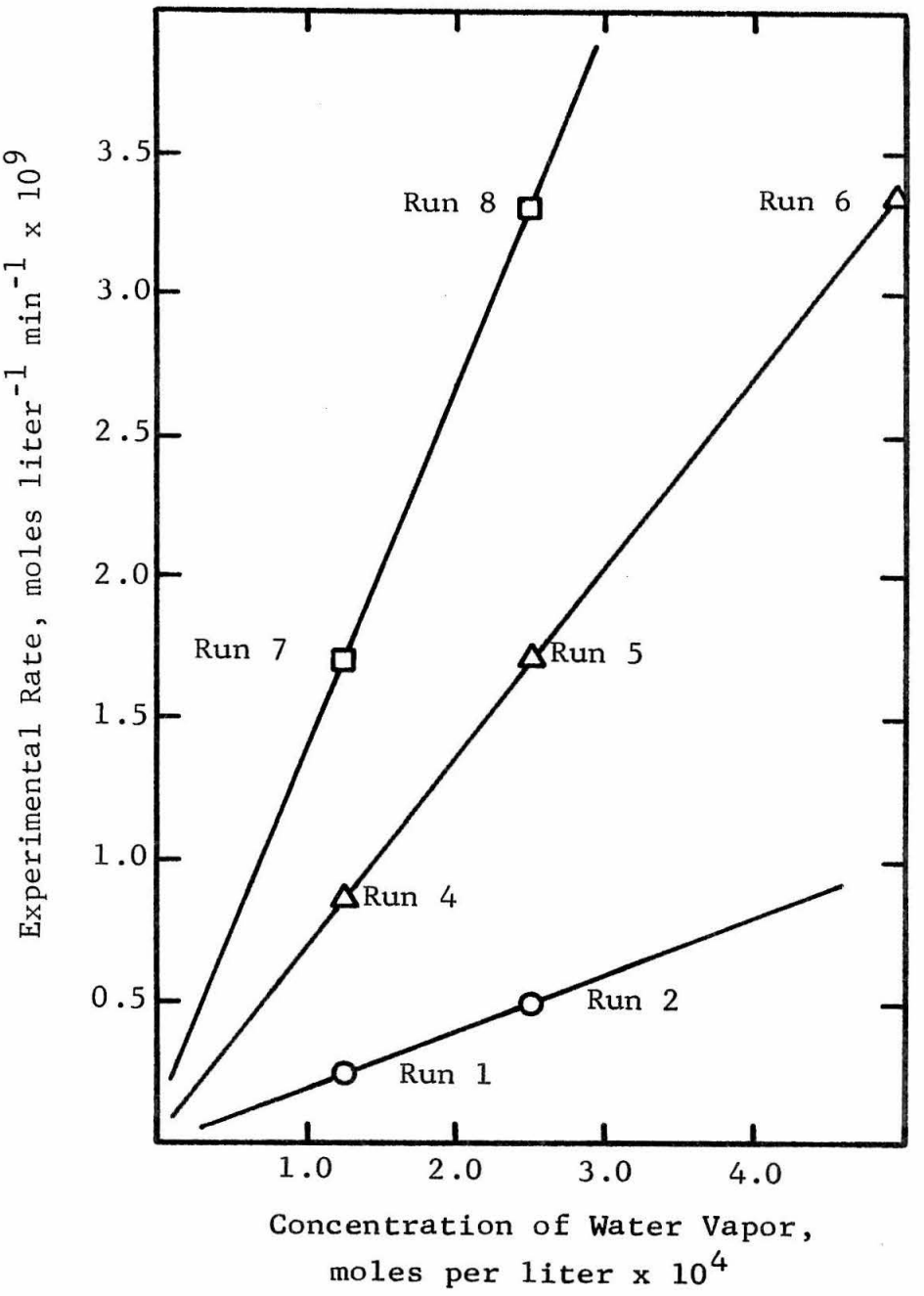


Figure 9. Determination of the Order of Reaction with Respect to Water Vapor: Linearity with the Origin Shows First-Order Behavior. Temp = 25°C.

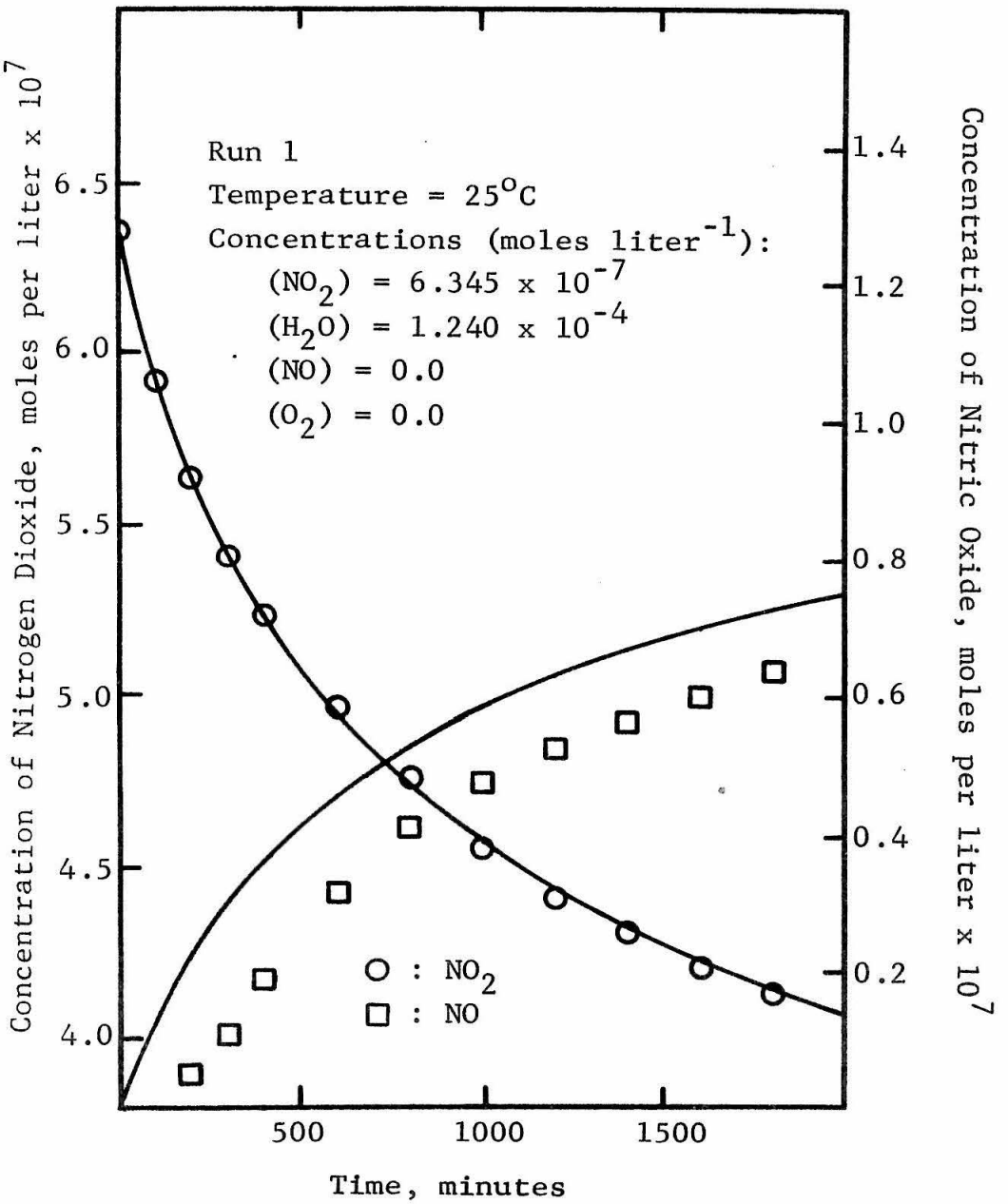


Figure 10. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 1 at 25°C.

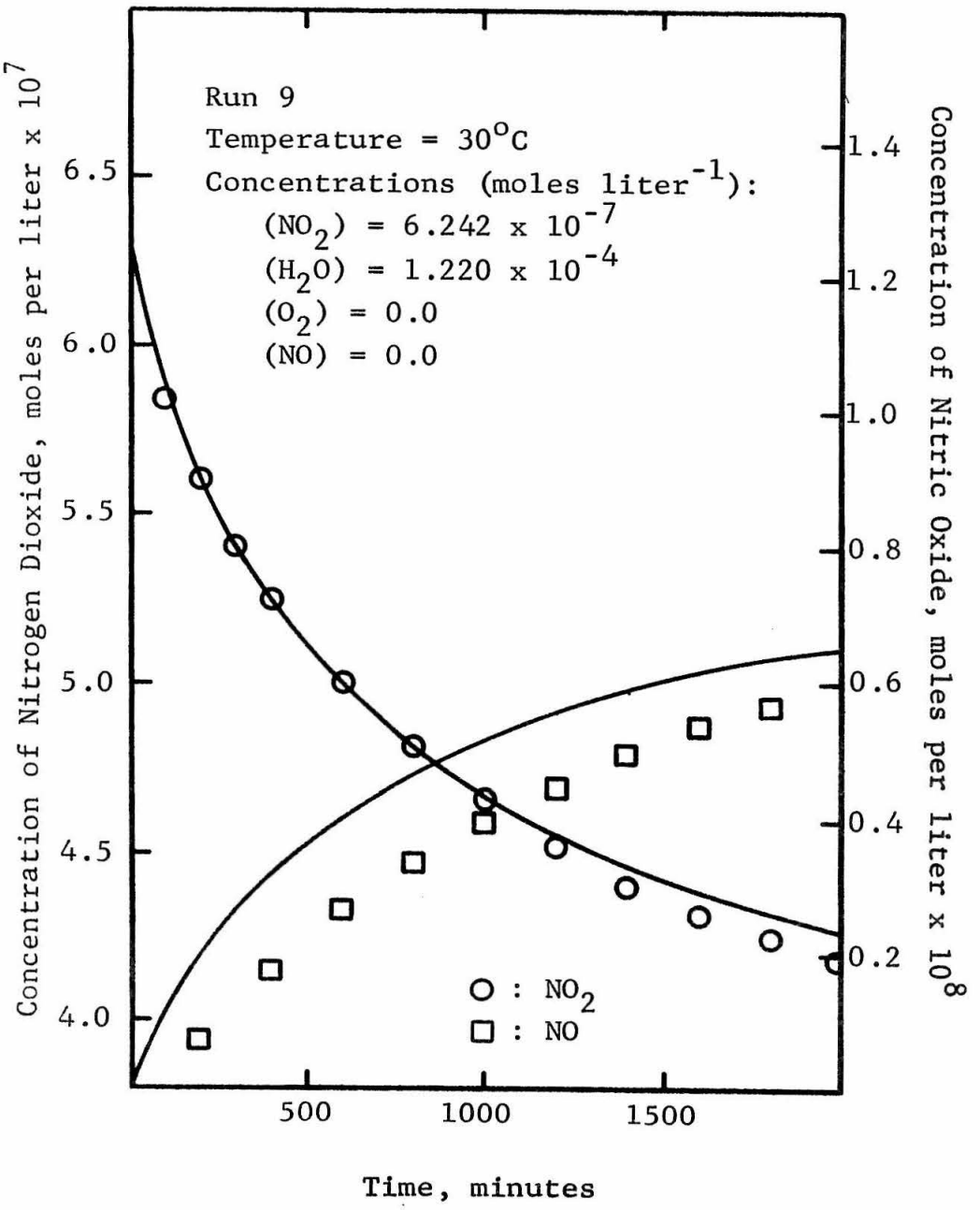


Figure 11. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 9 at 30°C.

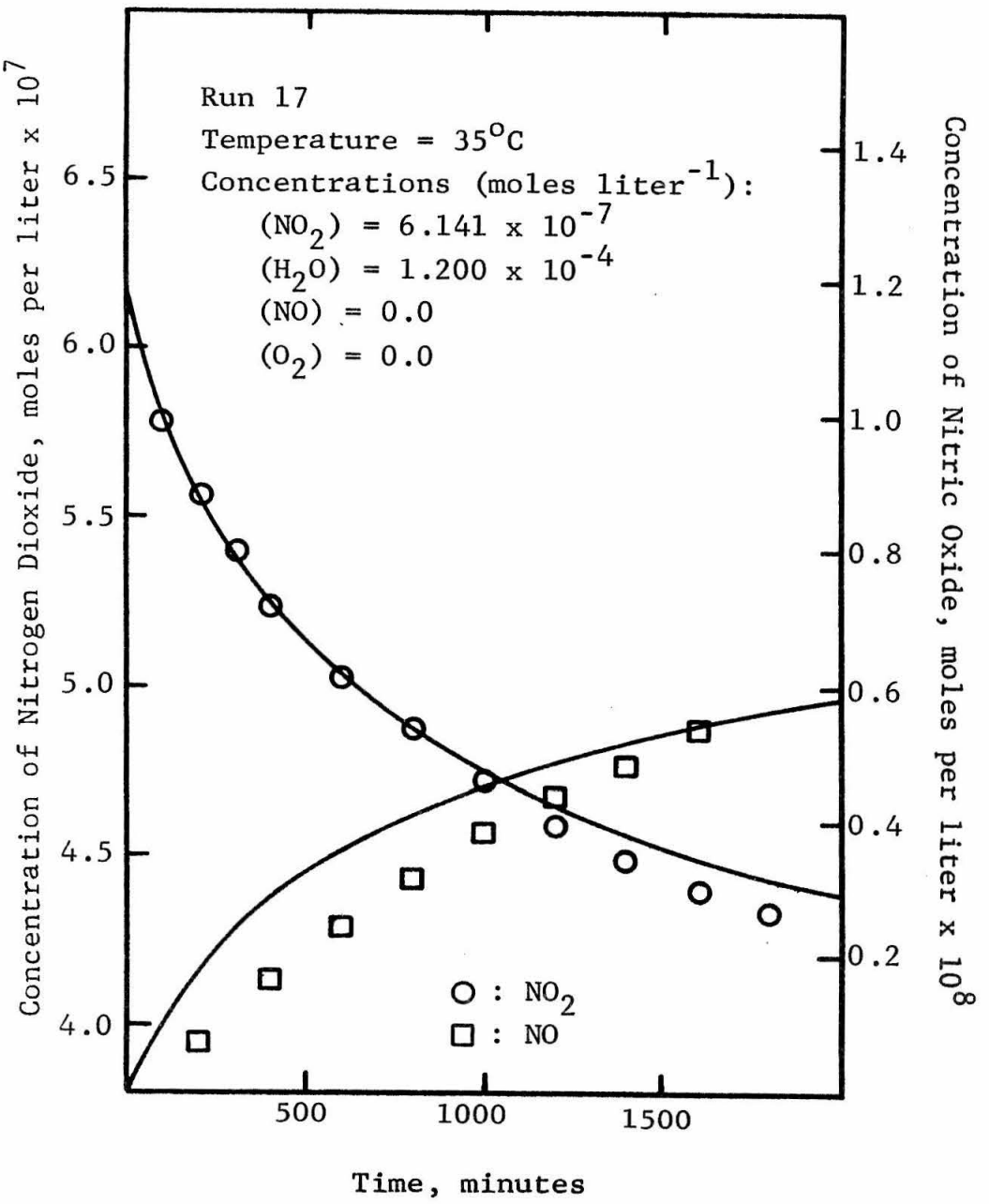


Figure 12. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 17 at 35°C.

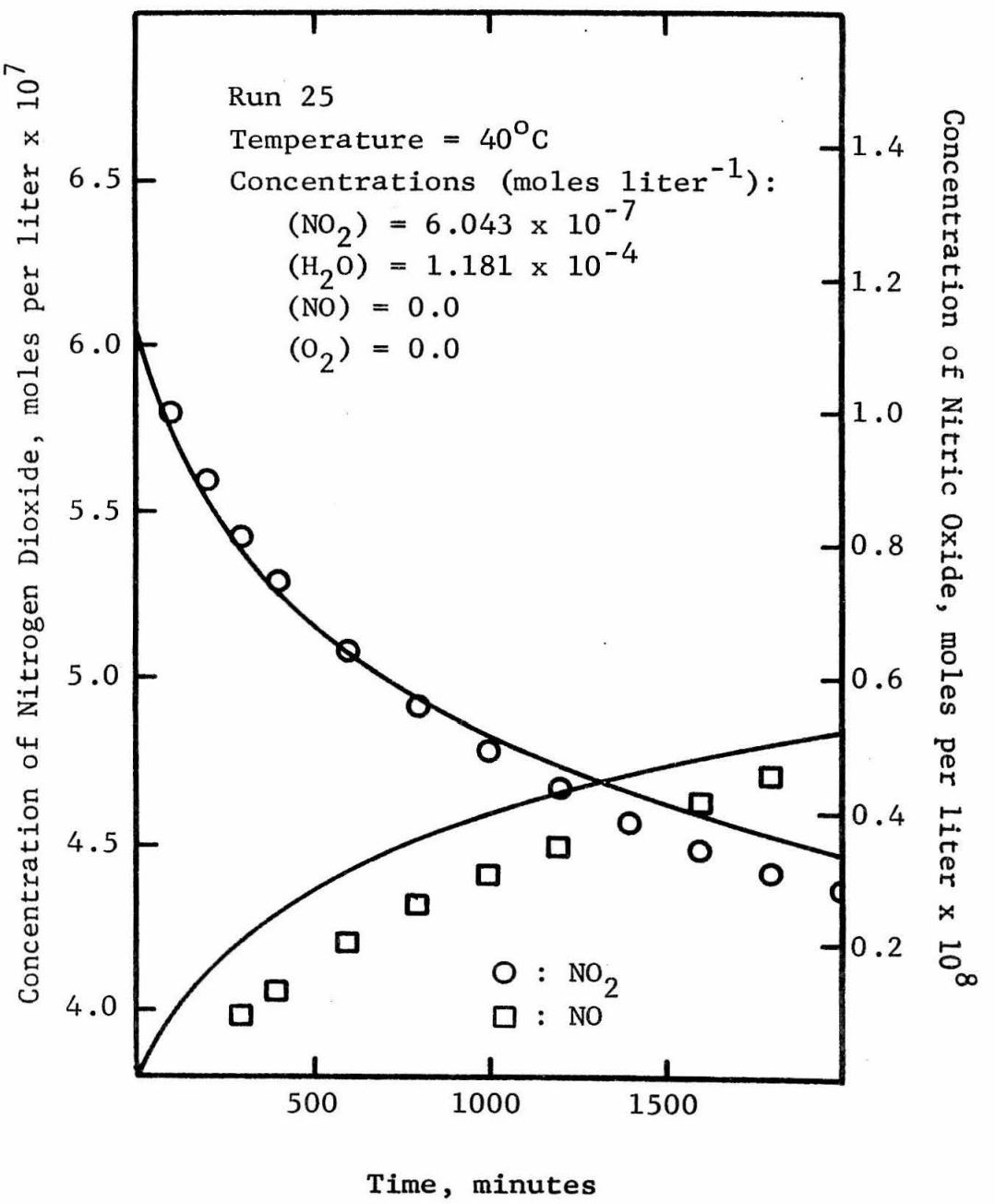


Figure 13. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 25 at 40°C.

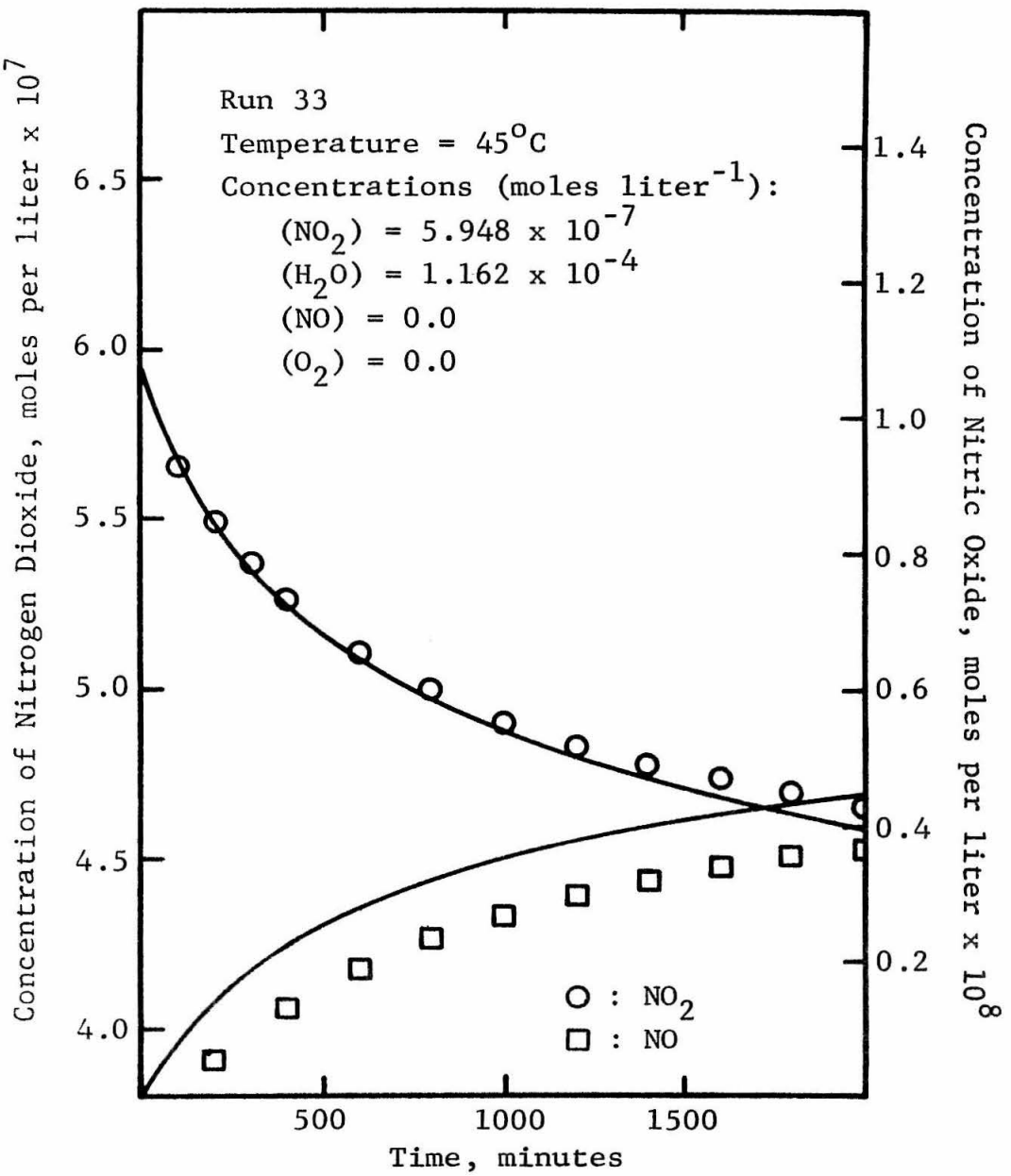


Figure 14. Time-Concentration Profiles for Nitric Oxide and Nitrogen Dioxide: Run 33 at 45°C.

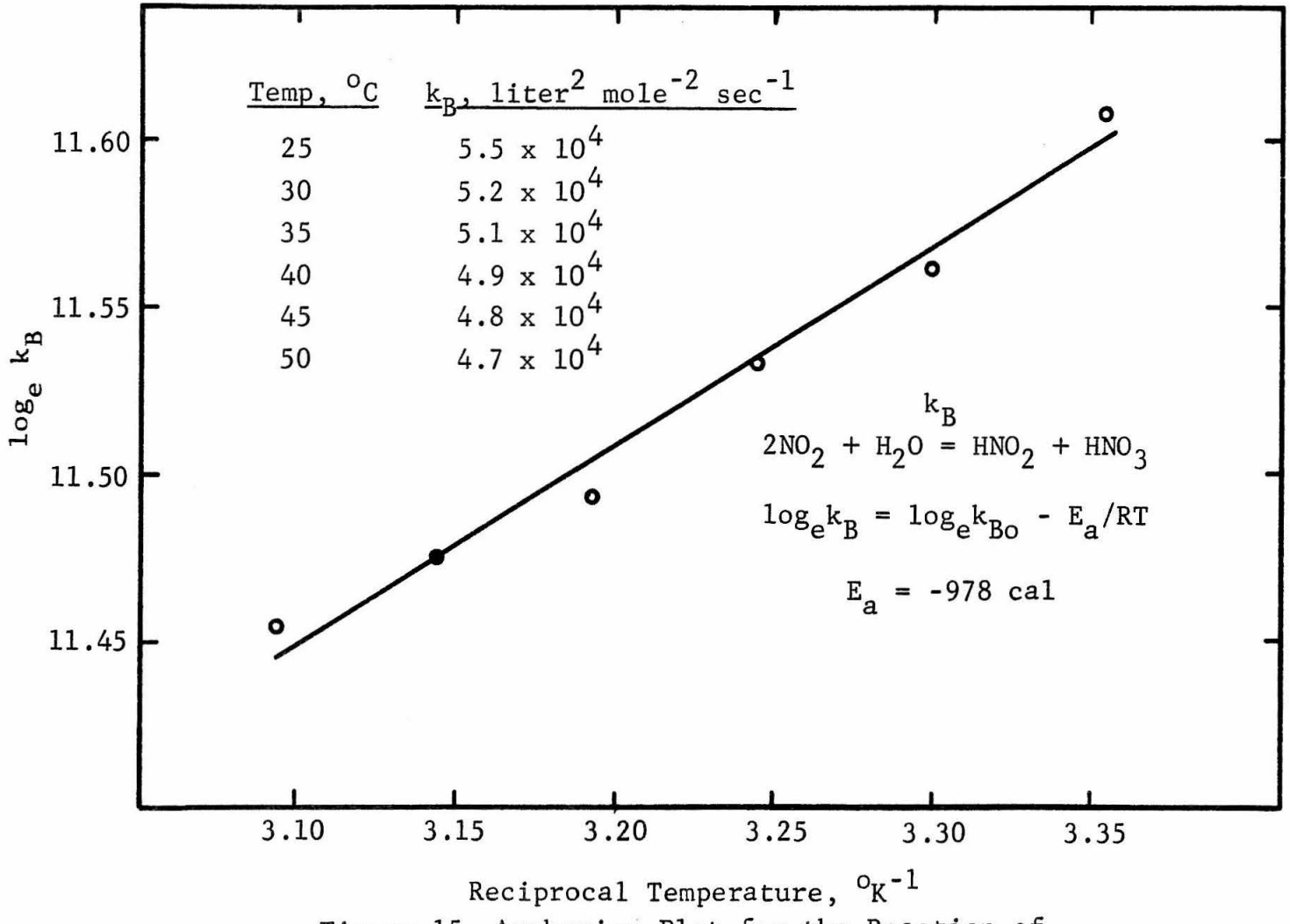


Figure 15. Arrhenius Plot for the Reaction of Nitrogen Dioxide with Water Vapor

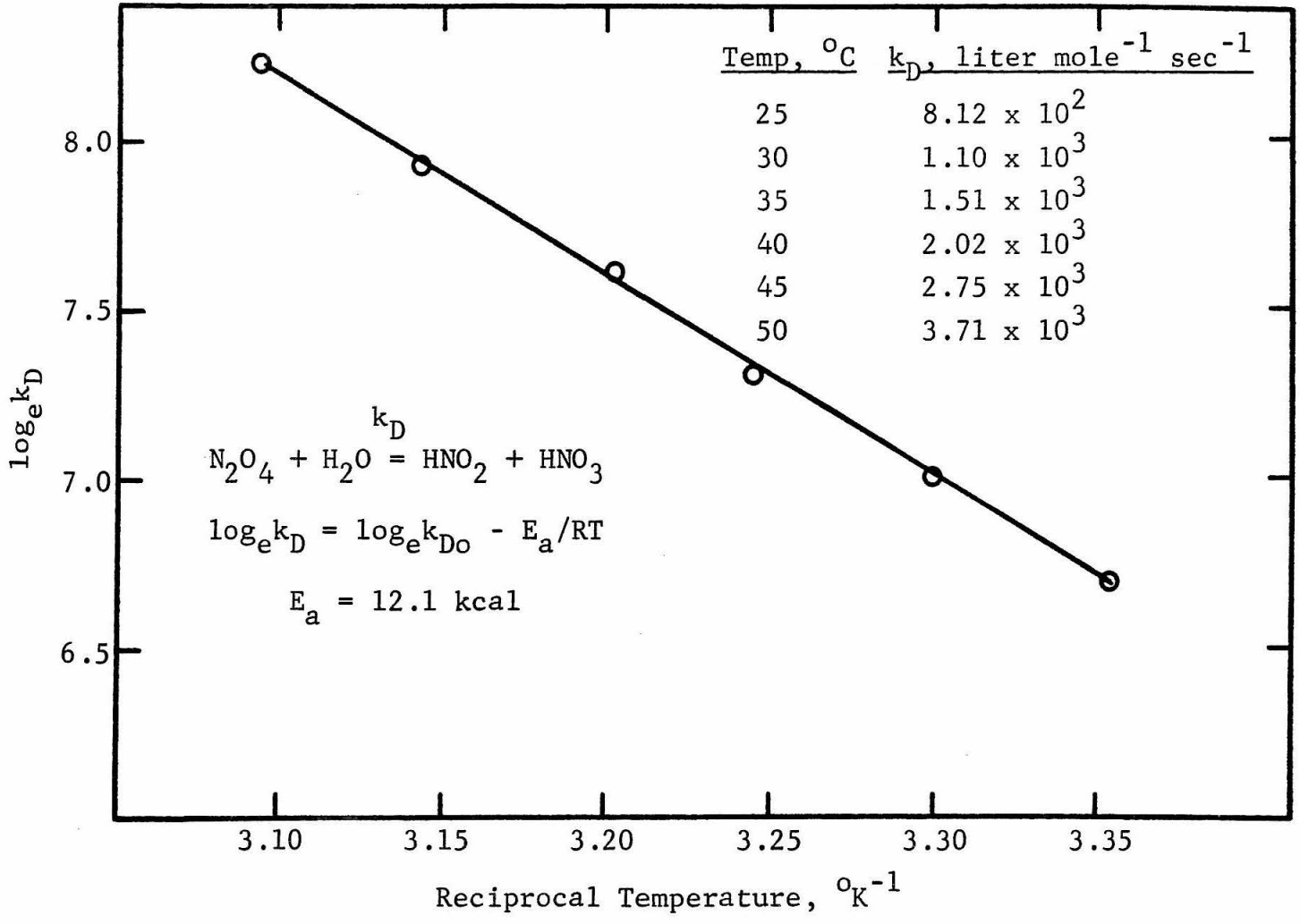


Figure 16. Arrhenius Plot for the Reaction of Dinitrogen Tetroxide with Water Vapor.

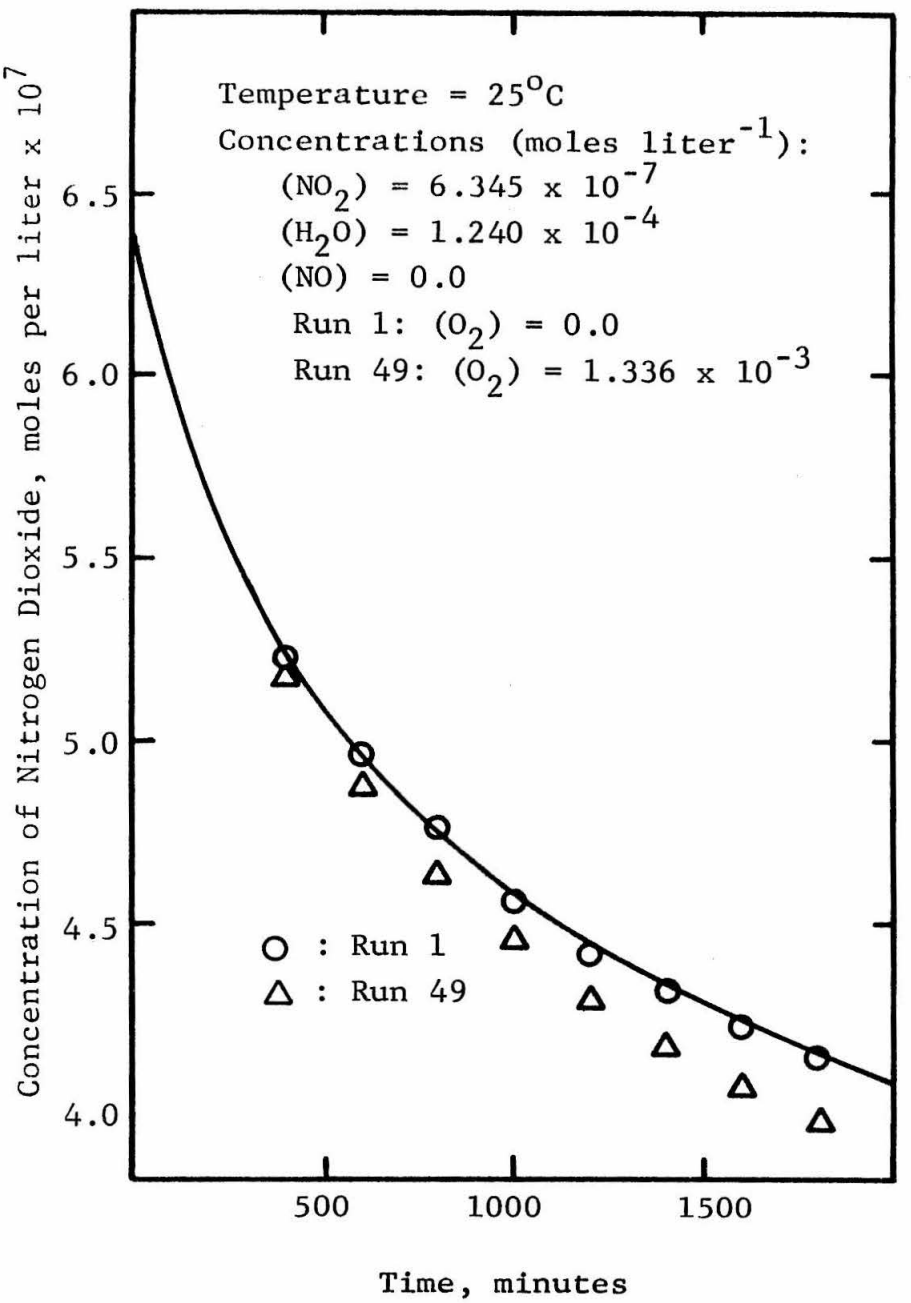


Figure 17. Dependence on Oxygen of the Reaction of Nitrogen Dioxide with Water Vapor at 25°C.

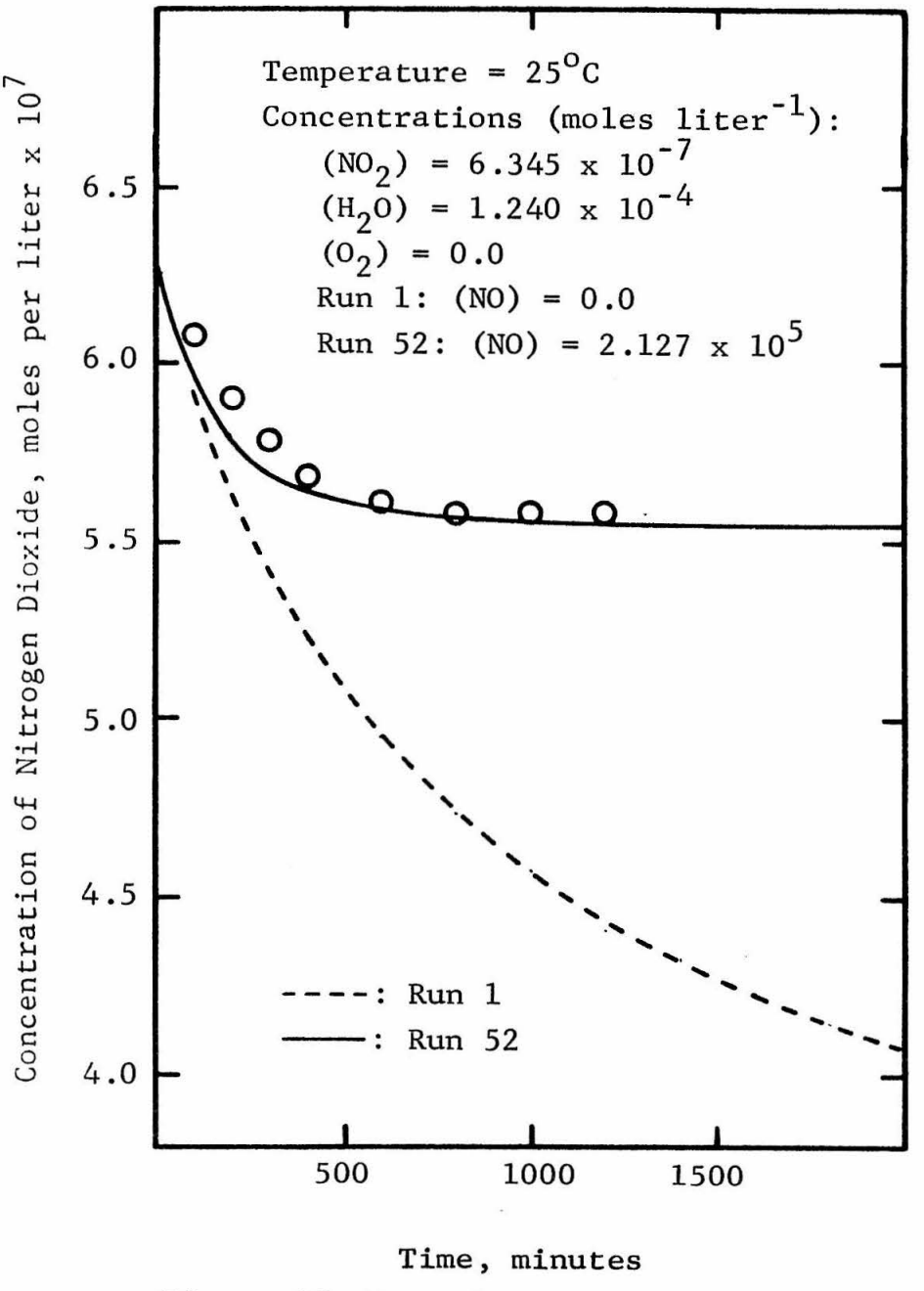


Figure 18. Dependence on Nitric Oxide of the Reaction of Nitrogen Dioxide with Water Vapor at 25°C.

Appendix A. Wet Chemical Analysis for Oxides of Nitrogen

APPENDIX A. WET CHEMICAL ANALYSIS

Summary

The wet chemical analysis of oxides of nitrogen by the phenol-disulfonic acid procedure is described. Some changes were made in the standard procedure (ASTM D-1608-60)[2] which improved the precision of the method.

Discussion

Two common chemical methods are used to measure ppm concentrations of the oxides of nitrogen in gaseous samples. They are the phenol-disulfonic acid procedure (ASTM D-1608-60), and the modified Griess-Ilosvay reaction (the Saltzman procedure, ASTM D-1607-60)[2]. The former method is particularly suited to analyze batch samples. The latter is better suited to samples of large volume which can be bubbled through absorbing solutions.

In the present work, the phenol-disulfonic acid procedure was used to analyze mixtures of nitrogen dioxide in nitrogen. Basically, the procedure consists of the following steps:

1. Absorbing nitrogen dioxide (or nitric oxide) into a solution containing hydrogen peroxide and sulfuric acid.
2. Neutralizing this solution with sodium hydroxide.
3. Evaporating the resulting solution to dryness.
4. Reacting the residue with phenol-disulfonic acid.

5. Forming a colored product by adding ammonium hydroxide.
6. Filtering the solutions.
7. Measuring the absorbance of the solutions.

The absorbance of the indicating solutions was measured at 400 millimicrons with a Beckman DU spectrophotometer. The slit width was 0.1 mm. A one-cm absorbing cell was used in conjunction with a tungsten light source.

Filtering of the solutions was eliminated in the present studies. It was found that a scatter of results of more than 20 ppm resulted from filtering. Instead, the indicating solutions were allowed to stand overnight. This procedure allowed any residue to settle. In addition, the colored product appeared to develop more completely when allowed to stand overnight. The standard gas mixture of nitrogen dioxide in nitrogen was found to contain 186.4 ($\pm$ 1.5) ppm of nitrogen dioxide. The standard deviation of 1.5 ppm was considered excellent in view of the scatter encountered before the new procedure was followed. The ASTM standard reports that the D-1608-60 procedure should give a repeatability of one percent of the mean for inorganic nitrates, and of five percent for automotive exhaust.

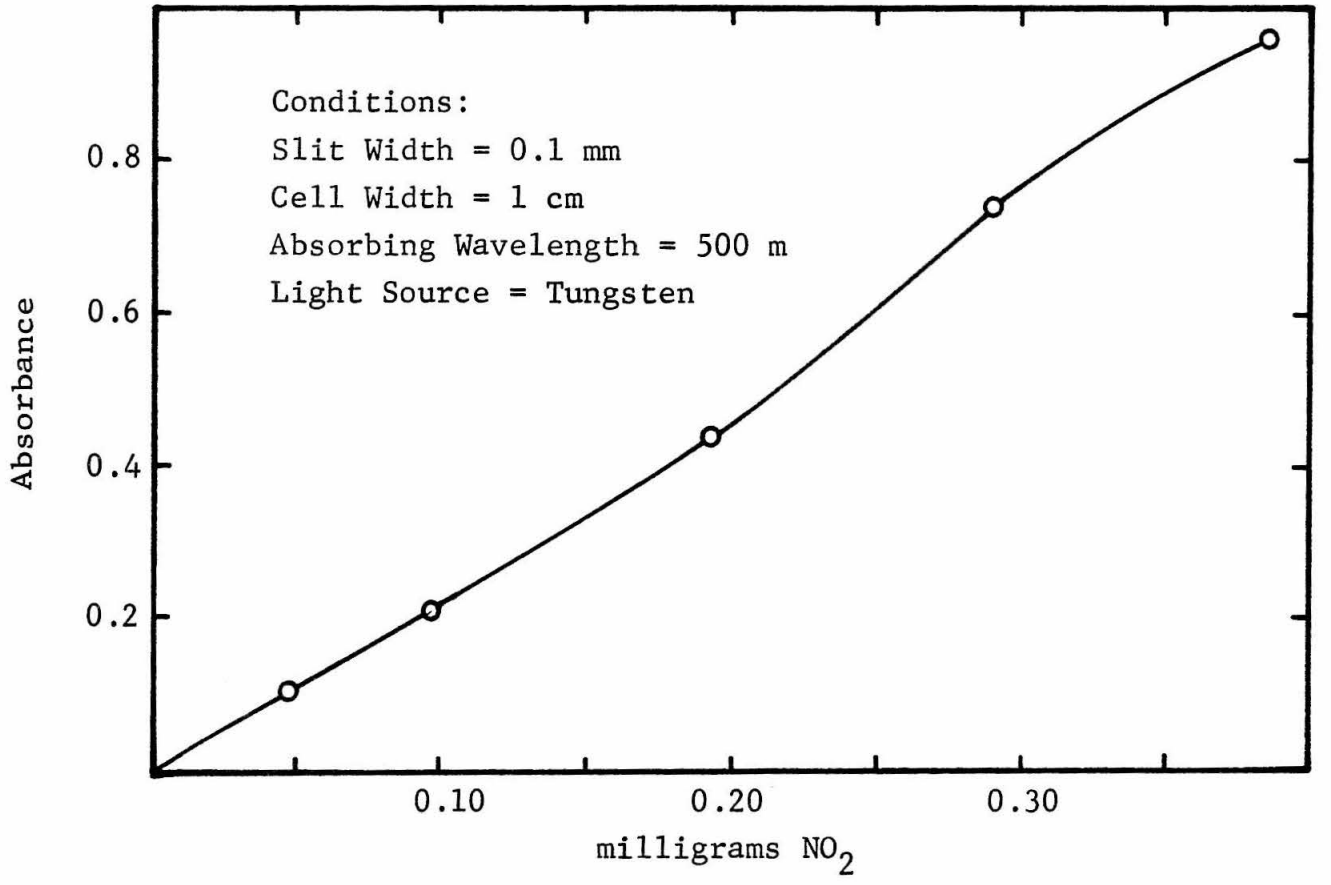


Figure 1. Sample Calibration of the Beckman DU Spectrophotometer for Nitrogen Dioxide: Revised Procedure.

Appendix B. Electron-Capture Gas Chromatography

APPENDIX B. ELECTRON-CAPTURE GAS CHROMATOGRAPHY

Summary

The application of electron-capture gas chromatography to the analysis of nitric oxide and nitrogen dioxide is described. A nitrogen carrier gas and an applied DC voltage across the detector provided the greatest sensitivity for both oxides of nitrogen. The use of an argon carrier gas, or a mixture of argon and methane, gave unsatisfactory sensitivity. Experimental evidence suggests that impurities in the nitrogen are responsible for the excellent response obtained for nitric oxide and nitrogen dioxide.

Introduction

The electron-capture detector in gas chromatography is a relatively-sophisticated analytical tool. Although it is in common use, especially for determining very small amounts of chlorinated pesticides, the operation of the detector is largely empirical. For example, although a five-percent mixture of methane in argon is universally recommended for both carrier and scavenger gases for the electron-capture detector, work in this laboratory showed no difference in response for the mixture over that of pure argon. Clearly, the instrument deserves more investigation.

The operation and present theory regarding the detector have been described elsewhere[19,33]. Basically, the device consists of two electrodes enclosed in an air-tight

container and immersed in a nitrogen atmosphere. A tritium-impregnated titanium foil is placed on the cathode, and a small voltage (about 10 volts) is impressed across the electrodes. Electrons are emitted from the foil and are collected at the anode. These electrons are recognized as the background current, and are measured by means of an electrometer. A carrier gas sweeps through the detector, continuously replacing the gas. The gas has an average residence time in the detector. This characteristic time may be reduced, and the response of the detector sharpened, by adding an extra stream of gas to the detector. This is the scavenger gas.

The variables associated with the detector include the following:

1. The activity of the radioactive foil
2. The voltage across the detector
    a. DC or DC pulse
    b. DC amplitude, pulse width, pulse height
3. The carrier gas
    a. Purity of the gas
    b. Composition of the gas
4. Carrier gas flow rate
5. Scavenger gas flow rate
6. Detector temperature.

Each of these variables contributes to the sensitivity of the detector to a large degree. Each may determine to which compounds the detector will respond, and in what relative

degree it will respond. The number of variables associated with the detector in addition to those associated with the chromatographic column provide great difficulty in operation, but provide great opportunities for enhancing its application. In the present work, interest centered primarily on the detection of nitric oxide and nitrogen dioxide in a nitrogen atmosphere.

Experimental

The detector was operated at 200°C, the maximum allowable for tritium-impregnated foil. Carrier gas flowed at the rate of 100 ml min^{-1}, the point at which the column was most efficient. The scavenger gas flow rate was also set at 100 ml min^{-1}. The radioactivity of the foil was 200 millicuries.

Various combinations of carrier gases and applied potentials were tried to determine which ones gave acceptable responses to both nitric oxide and nitrogen dioxide. The results are summarized in Table 1. When a nitrogen carrier gas and a steady DC voltage was used, excellent sensitivity to both oxides was obtained. In addition, nitrogen from the reactor did not interfere with the chromatographic separation. Other combinations of voltage and carrier gas were unsuccessful, argon with a pulsed voltage being acceptable for nitrogen dioxide alone.

A DC power supply was built to supply a variable voltage

for the detector. The detector was then optimized with respect to nitrogen dioxide by changing the applied voltage. Figure 1 shows that the maximum response for nitrogen dioxide occurred at about 15 volts.

There was some evidence that, when nitrogen was used as a carrier gas, the response of the detector was due to impurities in the nitrogen. This was demonstrated by the following observations.

The gases used with an electron-capture detector must be free from water vapor to avoid anomalous peaks in the chromatogram. In the present system, traps filled with Molecular Sieve 5A were placed in the carrier and scavenger streams. The traps were activated by heating in situ at 300^{o}C while the gas flow was maintained at its normal rate. This procedure desorbed water as well as other gaseous impurities from the molecular sieves. As the trap was heated, the backround current in the detector fell to zero and remained "off" for several hours. Gradually, the backround current returned. This was associated with the complete desorption of gases on the molecular sieves. When the trap was cooled to room temperature, the backround current through the detector again fell to zero. This was unexpected since the trap should have its greatest efficiency for removing impurities just after being activated. After the trap cooled, a full 24 hours were required before the backround current reappeared, and at least 72 hours elapsed before full sensi-

tivity was restored.

The implication of these observations is that some compound, only slightly adsorbed on molecular sieves, is present in the nitrogen carrier and causes the backround current to appear in the detector. This is similar to the behavior of the helium ionization detector when an impurity is introduced into the carrier. The impurity in nitrogen is undoubtedly either oxygen or argon, both of which can be used to raise the backround current in the helium ionization detector. Since the nitrogen is believed to be 99.5 percent pure, the concentration of the impurity must be relatively small (less than about 1000 ppm).

The work with the electron-capture detector was centered primarily on obtaining a working analysis and not on examining the variables associated with electron-capture gas chromatography. However, the method deserves a detailed investigation to develop the full potential of the technique.

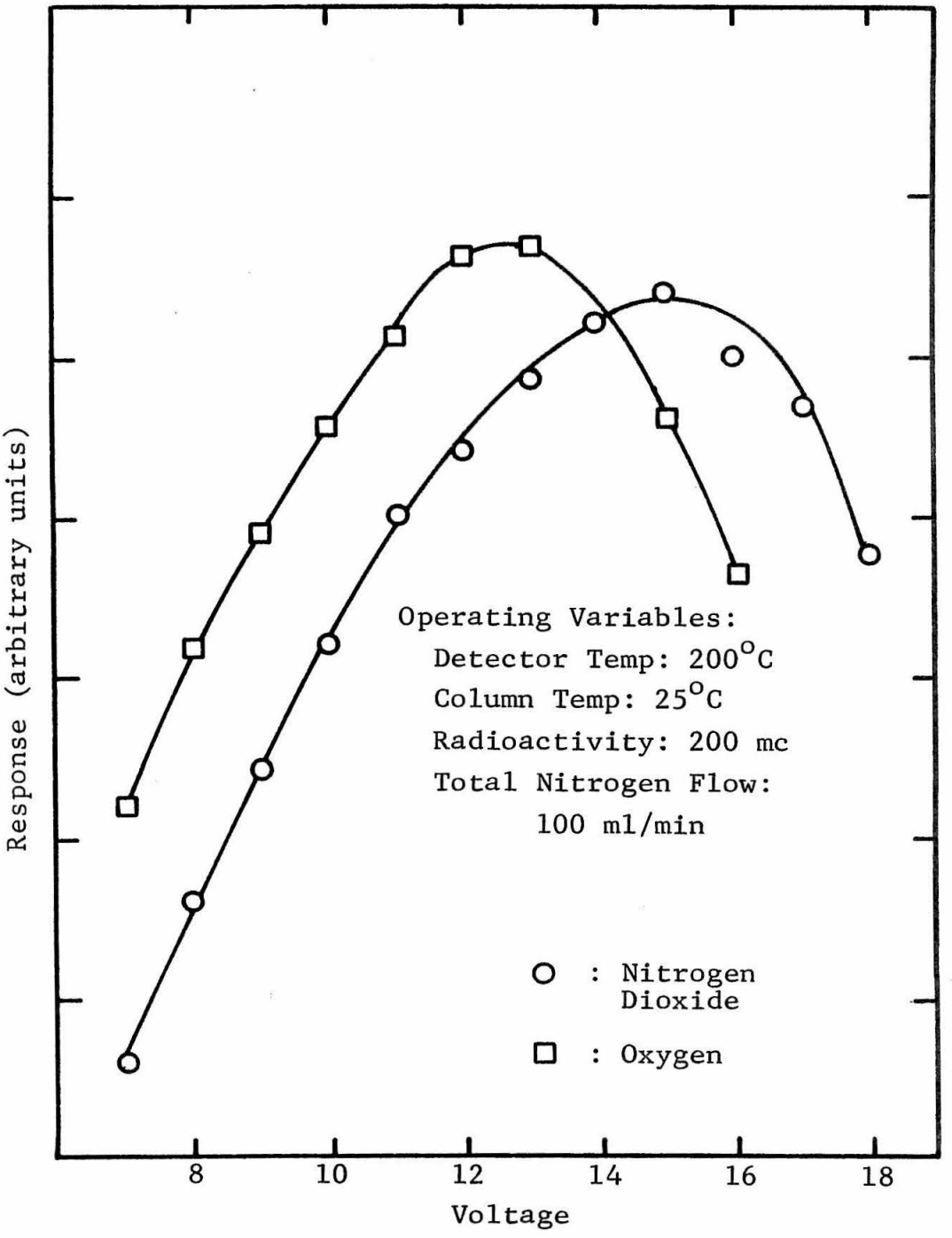


Figure 1. Optimization of the Electron-Capture Detector with Respect to Oxygen and Nitrogen Dioxide.

Appendix C. A Discrete-Sample Electrolytic Hygrometer

APPENDIX C. A DISCRETE-SAMPLE ELECTROLYTIC HYGROMETER

Summary

A microhygrometer was built to measure ppm concentrations of water in small gaseous samples. The instument was capable of measuring concentrations of water less than 5 ppm in 0.5 ml samples. The sensitivity was limited at this level by diffusion of water through connections in the hygrometer.

A section of the cell used in the Moisture Monitor, a moisture detector marketed by Consolidated Electrodynamics Corporation, was obtained from the company and adapted to the transient analysis of small gas samples. The cell is described in detail below. Basically, it consisted of a short length of glass tubing, inside of which were two platinum wires attached to the glass. A thin layer of P_2O_5 was deposited between the wires, on the glass. Water passing through the cell is adsorbed on the P_2O_5 and, when a DC potential is applied across the wires, the water is electrolyzed. The electrolysis current gives a quantitative determination of water entering the cell.

Apparatus

The hygrometer consisted of a 7-cm length of 1/10-inch o.d. glass tubing, inside of which are two parallel, helically-wound platinum wires affixed to the glass. The glass tubing and the wires were connected to 1/8-inch Swagelock

unions by means of machined Teflon inserts and sleeves. A platinum wire was silver-soldered onto each union. The unions were stainless steel, and served both as electrical contacts, and as a means to insert the cell into the analytical system. To prevent fracture, the hygrometer was tightly fit into a 1/2-inch hole bored in a one-inch Lucite rod. The hole was then filled with epoxy.

The hygrometer was connected electrically to a recording circuit. The circuit provided the voltage across the cell to electrolyze the water, and provided a properly attenuated signal to a one-mv potentiometric recorder. The electrolyzing voltage was set arbitrarily at 27 volts.

Before use, the hygrometer was coated with a thin film of P_2O_5. This treatment was performed before the Swagelock unions were attached, since the unions added some dead volume to the cell. First, the cell was flushed with reagent-grade acetone and dried with dry nitrogen. A coating solution was prepared which consisted of two parts of chemically-pure, concentrated phosphoric acid to eight parts of acetone, by volume. The cell was filled with the solution with a hypodermic syringe. Next, dry nitrogen was forced through the cell to drain it and to remove the bulk of the acetone. It was important to remove the acetone before drying the cell, since the heat generated in the cell during the drying-out procedure may decompose the acetone.

A low voltage was then applied across the cell while

nitrogen was forced through it. The drying procedure took several hours to complete the reaction

$$2H_3PO_4 = P_2O_5 \cdot 3H_2O = P_2O_5 + 3H_2 + 3/2\ O_2 \quad .$$

A Loenco L-206-6 linear "o"-ring switching valve with Viton-A o-rings was used to inject samples into the hygrometer. The six-port valve was connected to the reactor, to the inlet carrier stream, to a vacuum pump, to and from a 0.5 ml volume loop, and to the hygrometer.

Results

A typical hygrometer response is shown in Figure 1. The inflection near the middle of the trace occurred when the sample valve was set to refill the volume loop. The inflection was due to adsorbed water on the valve stem which was swept away by the dry carrier stream.

When operating continuously, the hygrometer had a leak rate of about 2 ppm of water. This was caused mainly by the diffusion of water through the O-rings of the valve. The leak rate was a reproducible function of temperature.

Conclusions

The hygrometer was useful in determining low concentrations of water in small samples. The response time was comparable to a chromatographic analysis. The sensitivity was superior to that of a chromatograph, the limiting value being about 0.1 ppm.

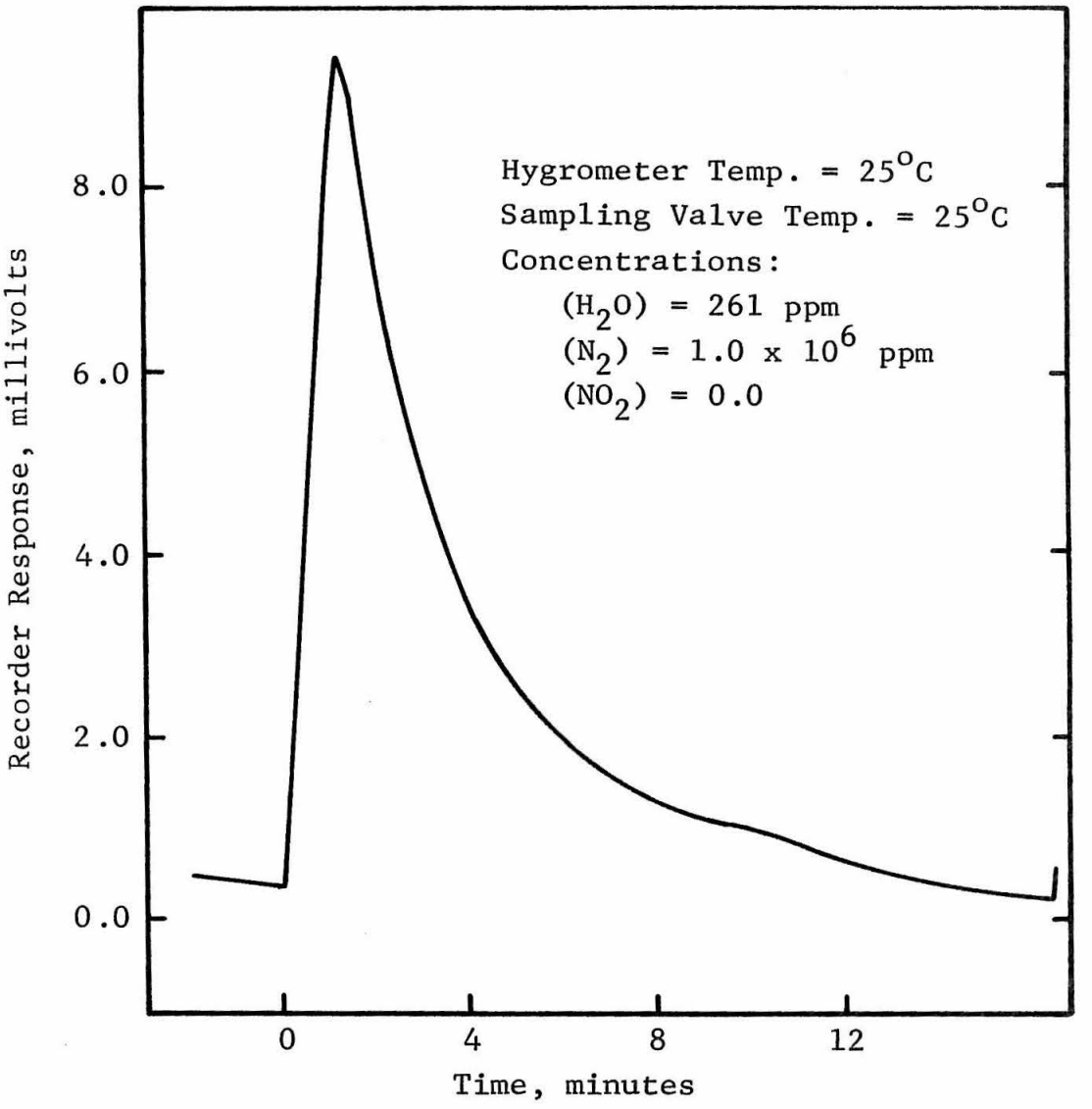


Figure 1. Typical Hygrometer Response to Water Vapor. Sample Size: 0.5 ml.

Appendix D. Experimental Data

Table 1. Summary of Initial Conditions for Experimental Runs

Run	Temp (°C)	Initial Concentrations (moles per liter) (NO_2) x10^6	(H_2O) x10^4	(O_2) x10^3	(NO) x10^5
1	25	0.6345	1.240	0.0	0.0
2	25	0.6345	2.481	0.0	0.0
4	25	1.269	1.240	0.0	0.0
5	25	1.269	2.481	0.0	0.0
6	25	1.269	4.962	0.0	0.0
7	25	1.842	1.240	0.0	0.0
8	25	1.842	2.481	0.0	0.0
9	30	0.6242	1.220	0.0	0.0
10	30	0.6242	2.440	0.0	0.0
12	30	1.248	1.220	0.0	0.0
13	30	1.248	2.440	0.0	0.0
14	30	1.248	4.880	0.0	0.0
17	35	0.6141	1.200	0.0	0.0
18	35	0.6141	2.400	0.0	0.0
19	35	0.6141	4.801	0.0	0.0
20	35	1.228	1.200	0.0	0.0
21	35	1.228	2.400	0.0	0.0
22	35	1.228	4.801	0.0	0.0
25	40	0.6043	1.181	0.0	0.0
26	40	0.6043	2.362	0.0	0.0
27	40	0.6043	4.724	0.0	0.0

Table 1 (contd)

Initial Concentrations (moles per liter)

Run	Temp (^{o}C)	(NO_2) x10^6	(H_2O) x10^4	(O_2) x10^3	(NO) x10^5
28	40	1.209	1.181	0.0	0.0
29	40	1.209	2.362	0.0	0.0
30	40	1.209	4.724	0.0	0.0
31	40	1.813	1.181	0.0	0.0
32	40	1.813	2.362	0.0	0.0
33	45	0.5948	1.162	0.0	0.0
34	45	0.5948	2.325	0.0	0.0
35	45	0.5948	4.650	0.0	0.0
36	45	1.190	1.162	0.0	0.0
37	45	1.190	2.325	0.0	0.0
38	45	1.190	4.650	0.0	0.0
39	45	1.784	1.162	0.0	0.0
40	45	1.784	2.325	0.0	0.0
45	50	1.171	1.144	0.0	0.0
46	50	1.171	2.289	0.0	0.0
47	50	1.757	1.144	0.0	0.0
48	50	1.757	2.289	0.0	0.0
49	25	0.6345	1.240	1.336	0.0
50	25	0.6345	2.481	1.336	0.0
51	25	0.6345	4.962	1.336	0.0

Table 1 (contd)

Run	Temp (°C)	Initial Concentrations (moles per liter) (NO_2) x10^6	(H_2O) x10^4	(O_2) x10^3	(NO) x10^5
52	25	0.6345	1.240	0.0	2.127
53	25	1.269	1.240	0.0	2.127
54	25	1.842	1.240	0.0	2.127

Run 1

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.347	0.0	6.347	0.0	0.0
50		6.10	0.576	6.106	3.391	0.149
100	1.63	5.91	1.208	5.922	3.116	0.273
150	3.22	5.76	1.746	5.765	2.890	0.378
200	4.81	5.65	2.211	5.630	2.702	0.469
300	1.06	5.40	2.982	5.404	2.404	0.620
400	1.82	5.22	3.600	5.224	2.179	0.742
500	2.51	5.08	4.112	5.074	2.002	0.842
600	3.13	4.96	4.546	4.946	1.859	0.928
800	4.11	4.76	5.250	4.739	1.641	1.066
1000	4.73	4.56	5.804	4.576	1.482	1.176
1200	5.22	4.41	6.257	4.443	1.360	1.265
1400	5.62	4.31	6.637	4.330	1.263	1.340
1600	5.99	4.21	6.964	4.234	1.182	1.404
1800	6.34	4.13	7.247	4.150	1.159	1.461
2000	6.63	4.04	7.550	4.087		1.508

Run 2

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 2.481 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.347	0.0	6.347	0.0	0.0
50		5.90	1.178	5.903	4.542	2.809
100		5.59	2.262	5.588	4.005	4.925
150		5.34	3.118	5.340	3.600	6.596
200	0.11	5.13	3.816	5.136	3.282	7.961
300	0.18	4.81	4.899	4.821	2.816	1.008
400	0.24	4.60	5.711	4.584	2.489	1.167
500	0.30	4.42	6.351	4.397	2.246	1.293
600	0.35	4.28	6.873	4.244	2.057	1.395
800	0.44	4.02	7.684	4.006	1.782	1.554
1000	0.50	3.80	8.293	3.827	1.591	1.675
1200	0.56	3.66	8.774	3.686	1.448	1.769
1400	0.60	3.53	9.166	3.570	1.346	1.847
1600	0.64	3.43	9.544	3.459	1.239	1.921
1800	0.68	3.34	9.817	3.379	1.168	1.975
2000	0.71	3.26	1.005	3.309	1.101	2.022

Run 4

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.269 \times 10^{-6}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.269	0.0	1.269	0.0	0.0
50		1.18	0.242	1.184	6.231	0.545
100		1.12	0.442	1.126	5.402	0.938
150	0.14	1.08	0.596	1.081	4.807	1.240
200	0.19	1.04	0.719	1.044	4.356	1.483
300	0.31	0.98	0.909	0.989	3.717	1.854
400	0.42	0.94	1.049	0.948	3.282	2.132
500	0.52	0.90	1.160	0.915	2.963	2.350
600	0.63	0.88	1.251	0.888	2.719	2.529
800	0.82	0.84	1.392	0.847	2.367	2.808
1000	1.00	0.81	1.499	0.815	2.123	3.019
1200	1.15	0.79	1.584	0.789	1.942	3.188
1400	1.28	0.78	1.654	0.769	1.802	3.326
1600	1.38	0.76	1.714	0.752	1.622	3.444
1800	1.46	0.75	1.764	0.737	1.598	3.544
2000	1.50	0.74	1.808	0.724	1.522	3.631

Run 5

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.269 \times 10^{-6}$

$[H_2O] = 2.481 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.269	0.0	1.269	0.0	0.0
50		1.13	0.452	1.117	8.008	0.984
100	0.14	1.02	0.763	1.027	6.563	1.591
150	0.21	0.95	0.979	0.964	5.632	2.015
200	0.31	0.92	1.142	0.916	4.977	2.333
300	0.54	0.86	1.374	0.848	4.114	2.790
400	0.80	0.81	1.536	0.801	3.564	3.108
500	1.04	0.78	1.658	0.765	3.181	3.348
600	1.24	0.75	1.754	0.737	2.896	3.537
800	1.50	0.70	1.898	0.694	2.500	3.821
1000	1.71	0.67	2.002	0.664	2.236	4.027
1200	1.85	0.64	2.082	0.640	2.040	4.185
1400	1.96	0.62	2.146	0.621	1.902	4.311
1600	2.04	0.59	2.198	0.606	1.790	4.414
1800	2.10	0.58	2.241	0.593	1.699	4.500
2000	2.12	0.56	2.278	0.582	1.625	4.572

Run 6

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.269 \times 10^{-7}$

$[H_2O] = 4.962 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.269	0.0	1.269	0.0	0.0
50		1.02	0.792	1.012	9.784	1.682
100	0.14	0.88	1.218	0.888	7.489	2.512
150	0.26	0.80	1.483	0.812	6.185	3.027
200	0.45	0.75	1.667	0.758	5.339	3.387
300	0.85	0.70	1.912	0.687	4.301	3.866
400	1.22	0.65	2.072	0.640	3.682	4.190
500	1.46	0.61	2.186	0.607	3.269	4.405
600	1.65	0.58	2.273	0.581	2.973	4.576
800	1.94	0.54	2.397	0.545	2.576	4.821
1000	2.15	0.51	2.483	0.520	2.322	4.990
1200	2.31	0.50	2.545	0.501	2.146	5.111
1400	2.41	0.49	2.592	0.487	2.017	5.204
1600	2.48	0.48	2.630	0.478	1.912	5.270
1800	2.53	0.48	2.658	0.468	1.845	5.335
2000	2.54	0.47	2.682	0.461	1.784	5.381

Run 7

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.842 \times 10^{-6}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.842	0.0	1.842	0.0	0.0
50		1.76	0.492	1.677	8.448	1.070
100	0.24	1.56	0.846	1.574	7.050	1.762
150	0.43	1.47	1.100	1.500	6.128	2.262
200	0.64	1.41	1.296	1.442	5.470	2.647
300	0.94	1.34	1.584	1.358	4.584	3.215
400	1.21	1.29	1.792	1.296	4.009	3.624
500	1.44	1.24	1.952	1.249	3.602	3.940
600	1.62	2.21	2.080	1.211	3.297	4.194
800	1.88	1.16	2.278	1.153	2.865	4.584
1000	2.10	1.11	2.424	1.109	2.572	4.874
1200	2.27	1.08	2.539	1.076	2.358	5.102
1400	2.40	1.06	2.633	1.048	2.194	5.287
1600	2.50	1.05	2.710	1.025	2.064	5.442
1800	2.55	1.03	2.776	1.005	1.959	5.572
2000	2.58	1.01	2.833	0.988	1.871	5.685

Run 8

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.842 \times 10^{-6}$

$[H_2O] = 2.481 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.842	0.0	1.842	0.0	0.0
50		1.59	0.883	1.556	1.055	1.871
100	0.41	1.41	1.395	1.407	0.828	2.873
150	0.63	1.29	1.728	1.310	0.695	3.525
200	0.84	1.23	1.967	1.240	0.607	3.995
300	1.22	1.15	2.298	1.143	0.496	4.645
400	1.52	1.09	2.521	1.077	0.428	5.086
500	1.78	1.04	2.686	1.029	0.381	5.410
600	2.00	1.01	2.814	0.991	0.348	5.663
800	2.39	0.95	3.002	0.935	0.302	6.035
1000	2.71	0.90	3.136	0.896	0.272	6.299
1200	2.93	0.85	3.236	0.866	0.250	6.497
1400	3.08	0.81	3.314	0.843	0.234	6.652
1600	3.18	0.79	3.377	0.824	0.222	6.776
1800	3.26	0.77	3.428	0.809	0.212	6.878
2000	3.34	0.76	3.471	0.797	0.205	6.972

Run 9

Initial Conditions:

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.242 \times 10^{-7}$

$[H_2O] = 1.220 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.242	0.0	6.242	0.0	0.0
50		6.02	0.511	6.024	3.211	0.134
100	0.30	5.84	1.076	5.861	2.940	0.244
150	0.50	5.72	1.552	5.722	2.720	0.338
200	0.71	5.60	1.963	5.602	2.538	0.418
300	1.22	5.40	2.640	5.405	2.256	0.551
400	1.74	5.24	3.182	5.247	2.044	0.657
500	2.25	5.11	3.631	5.115	1.880	0.745
600	2.67	5.00	4.011	5.004	1.748	0.820
800	3.36	4.81	4.630	4.822	1.548	0.942
1000	3.93	4.66	5.119	4.678	1.403	1.038
1200	4.47	4.52	5.519	4.560	1.292	1.117
1400	4.92	4.40	5.856	4.461	1.204	1.183
1600	5.33	4.32	6.146	4.376	1.128	1.241
1800	5.65	4.25	6.399	4.299	1.193	1.292
2000		4.18	6.950	4.186	1.051	1.376

Run 10

Initial Conditions:

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.242 \times 10^{-7}$

$[H_2O] = 2.440 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.242	0.0	6.242	0.0	0.0
50		5.83	1.049	5.841	4.300	0.260
100	0.63	5.55	2.017	5.561	3.782	0.441
150	1.06	5.34	2.778	5.341	3.396	0.589
200	1.55	5.16	3.397	5.161	3.097	0.710
300	2.43	4.88	4.358	4.881	2.663	0.898
400	3.23	4.68	5.080	4.671	2.361	1.040
500	3.90	4.52	5.650	4.504	2.137	1.151
600	4.53	4.38	6.117	4.368	1.964	1.243
800	5.52	4.15	6.846	4.154	1.713	1.386
1000	6.25	3.95	7.397	3.992	1.538	1.495
1200	6.82	3.80	7.833	3.864	1.408	1.581
1400	7.29	3.67	8.189	3.759	1.321	1.651
1600	7.66	3.57	8.535	3.657	1.215	1.719
1800	8.05	3.48	8.784	3.584	1.152	1.768
2000	8.29	3.39	9.001	3.519	1.126	1.812

Run 12

Initial Conditions:

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.248 \times 10^{-6}$

$[H_2O] = 1.220 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.248	0.0	1.248	0.0	0.0
50		1.17	0.215	1.172	5.879	0.489
100	0.12	1.12	0.392	1.120	5.076	0.836
150	0.17	1.08	0.528	1.081	4.510	1.100
200	0.23	1.05	0.636	1.049	4.088	1.313
300	0.34	1.00	0.802	1.000	3.496	1.639
400	0.46	0.96	0.926	0.964	3.096	1.882
500	0.57	0.93	1.023	0.935	2.805	2.074
600	0.67	0.91	1.103	0.912	2.583	2.232
800	0.83	0.87	1.229	0.875	2.263	2.480
1000	0.97	0.84	1.324	0.847	2.042	2.669
1200	1.08	0.81	1.400	0.824	1.878	2.820
1400	1.20	0.79	1.463	0.806	1.768	2.944
1600	1.29	0.78	1.516	0.790	1.650	3.049
1800	1.36	0.76	1.562	0.776	1.545	3.139
2000	1.41	0.75	1.601	0.765	1.497	3.218

Run 13

Initial Conditions:

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.248 \times 10^{-6}$

$[H_2O] = 2.440 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.248	0.0	1.248	0.0	0.0
50		1.11	0.403	1.112	7.562	0.882
100	0.24	1.02	0.679	1.032	6.194	1.420
150	0.43	0.97	0.871	0.976	5.325	1.796
200	0.60	0.93	1.015	0.934	4.721	2.078
300	0.84	0.88	1.223	0.873	3.928	2.485
400	1.01	0.84	1.369	0.830	3.425	2.772
500	1.14	0.81	1.479	0.798	3.075	2.988
600	1.26	0.78	1.566	0.773	2.815	3.160
800	1.48	0.74	1.697	0.734	2.454	3.419
1000	1.64	0.71	1.792	0.706	2.213	3.607
1200	1.76	0.68	1.865	0.684	2.024	3.751
1400	1.84	0.67	1.923	0.667	1.908	3.866
1600	1.91	0.64	1.970	0.653	1.808	3.959
1800	1.96	0.62	2.010	0.642	1.726	4.037
2000	2.00	0.61	2.043	0.632	1.660	4.102

Run 14

Initial Conditions:

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.248 \times 10^{-6}$

$[H_2O] = 4.880 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.248	0.0	1.248	0.0	0.0
50	0.20	1.02	0.709	1.017	9.283	1.511
100	0.45	1.00	1.093	0.906	7.141	2.257
150	0.69	0.83	1.331	0.837	5.936	2.722
200	0.89	0.77	1.499	0.788	5.157	3.049
300	1.18	0.70	1.723	0.722	4.202	3.489
400	1.39	0.66	1.871	0.679	3.633	3.778
500	1.55	0.63	1.977	0.648	3.254	3.987
600	1.69	0.60	2.058	0.625	2.982	4.145
800	1.88	0.57	2.173	0.591	2.618	4.372
1000	2.02	0.54	2.252	0.568	2.386	4.527
1200	2.09	0.52	2.308	0.551	2.227	4.639
1400	2.15	0.51	2.351	0.538	2.112	4.723
1600	2.21	0.50	2.384	0.529	1.920	4.786
1800	2.25	0.49	2.413	0.526		4.817
2000	2.26	0.48				4.878

Run 17

Initial Conditions:

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.141 \times 10^{-7}$

$[H_2O] = 1.200 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.141	0.0	6.141	0.0	0.0
50		5.94	0.462	5.941	3.062	0.123
100	0.40	5.78	0.972	5.794	2.786	0.222
150	0.55	5.66	1.397	5.670	2.566	0.305
200	0.73	5.56	1.761	5.565	2.388	0.376
300	1.17	5.39	2.392	5.392	2.115	0.492
400	1.63	5.24	2.830	5.254	1.915	0.585
500	2.05	5.13	3.221	5.140	1.762	0.662
600	2.43	5.03	3.552	5.042	1.639	0.727
800	3.15	4.87	4.092	4.884	1.456	0.833
1000	3.82	4.72	4.518	4.759	1.323	0.917
1200	4.37	4.59	4.868	4.656	1.222	0.986
1400	4.82	4.48	5.163	4.569	1.142	1.004
1600	5.40	4.40	5.418	4.494	1.081	1.094
1800	5.95	4.33	5.653	4.435	0.905	1.136
2000		4.28	6.047	4.308		1.219

Run 18

Initial Conditions:

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.141 \times 10^{-7}$

$[H_2O] = 2.400 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.141	0.0	6.141	0.0	0.0
50		5.77	0.950	5.774	4.094	0.231
100	0.55	5.52	1.822	5.523	3.580	0.400
150	0.88	5.33	2.499	5.327	3.205	0.532
200	1.15	5.17	3.048	5.168	2.920	0.639
300	1.82	4.94	3.895	4.824	2.512	0.804
400	2.65	4.77	4.532	4.737	2.231	0.929
500	3.36	4.62	5.035	4.590	2.026	1.027
600	3.88	4.48	5.448	4.469	1.867	1.108
800	4.76	4.25	6.094	4.280	1.638	1.235
1000	5.42	4.09	6.584	4.136	1.479	1.332
1200	6.05	3.97	6.973	4.022	1.362	1.408
1400	6.54	3.85	7.291	3.927	1.334	1.472
1600	6.98	3.74	7.581	3.843	1.192	1.528
1800	7.35	3.65	7.806	3.776	1.141	1.572
2000	7.60	3.57	8.033	3.710	1.078	1.617

Run 19

Initial Conditions:

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.141 \times 10^{-7}$

$[H_2O] = 4.801 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.141	0.0	6.141	0.0	0.0
50		5.54	0.183	5.485	5.306	0.420
100		5.51	0.321	5.090	4.404	0.686
150		4.79	0.418	4.810	3.814	0.875
200	0.12	4.57	0.492	4.597	3.395	1.018
300	0.20	4.30	0.599	4.287	2.836	1.226
400	0.29	4.11	0.674	4.069	2.479	1.373
500	0.40	3.96	0.731	3.904	2.228	1.484
600	0.48	3.83	0.775	3.774	2.042	1.571
800	0.62	3.59	0.842	3.579	1.783	1.702
1000	0.73	3.43	0.890	3.438	1.611	1.796
1200	0.82	3.31	0.927	3.331	1.493	1.868
1400	0.88	3.21	0.959	3.237	1.385	1.931
1600	0.93	3.11	0.981	3.161		1.980
1800	0.97	3.00	1.004	3.103		2.021
2000	1.02		1.025	3.041		2.062

Run 20

Initial Conditions:

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.228 \times 10^{-6}$

$[H_2O] = 1.200 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.228	0.0	1.228	0.0	0.0
50		1.16	0.194	1.159	5.571	0.444
100		1.11	0.352	1.113	4.775	0.752
150	0.15	1.08	0.471	1.078	4.230	0.984
200	0.21	1.03	0.566	1.051	3.830	1.170
300	0.34	1.00	0.710	1.008	3.278	1.453
400	0.47	0.97	0.818	0.977	2.911	1.665
500	0.57	0.94	0.903	0.952	2.646	1.833
600	0.67	0.94	0.973	0.931	2.444	1.971
800	0.85	0.90	1.083	0.899	2.154	2.188
1000	0.99	0.87	1.167	0.874	1.955	2.354
1200	1.10	0.84	1.234	0.854	1.807	2.486
1400	1.18	0.83	1.289	0.838	1.692	2.596
1600	1.24	0.81	1.336	0.824	1.606	2.688
1800	1.28	0.80	1.376	0.812	1.528	2.767
2000	1.31	0.79	1.410	0.802	1.467	2.836

Run 21

Initial Conditions:

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.228 \times 10^{-6}$

$[H_2O] = 2.400 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.228	0.0	1.228	0.0	0.0
50		1.10	0.364	1.104	7.158	0.800
100		1.03	0.609	1.034	5.839	1.277
150	0.14	0.98	0.779	0.984	5.023	1.608
200	0.19	0.94	0.906	0.947	4.462	1.857
300	0.35	0.88	1.089	0.894	3.734	2.216
400	0.54	0.85	1.219	0.856	3.276	2.470
500	0.76	0.81	1.316	0.827	2.958	2.663
600	0.91	0.78	1.394	0.804	2.723	2.816
800	1.12	0.75	1.511	0.770	2.397	3.046
1000	1.28	0.72	1.596	0.745	2.179	3.214
1200	1.39	0.70	1.661	0.725	2.424	3.346
1400	1.49	0.68	1.713	0.710	1.910	3.444
1600	1.58	0.67	1.754	0.698	1.816	3.527
1800	1.65	0.66	1.790	0.690	1.741	3.583
2000	1.72	0.66	1.817	0.679	1.686	3.651

Run 22

Initial Conditions:

Reactor Temperature: $35.0^{o}C$

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.228 \times 10^{-6}$

$[H_2O] = 4.801 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.228	0.0	1.228	0.0	0.0
50		1.02	0.641	1.018	8.808	1.371
100	0.17	0.92	0.984	0.919	6.788	2.036
150	0.28	0.86	1.198	0.857	5.672	2.452
200	0.41	0.82	1.348	0.814	4.957	2.745
300	0.71	0.76	1.550	0.755	4.084	3.141
400	1.02	0.71	1.669	0.716	3.566	3.404
500	1.26	0.68	1.780	0.688	3.222	3.592
600	1.42	0.65	1.853	0.666	2.975	3.736
800	1.68	0.61	1.957	0.636	2.648	3.940
1000	1.82	0.58	2.027	0.615	2.441	4.078
1200	1.92	0.57	2.076	0.600	2.365	4.180
1400	1.98	0.56	2.113	0.589	2.202	4.248
1600	2.02	0.55	2.141	0.590	2.129	4.303
1800	2.04	0.53	2.162	0.575	2.220	4.346
2000	2.04	0.52	2.178	0.570	2.032	4.377

Run 25

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.043 \times 10^{-7}$

$[H_2O] = 1.181 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.043	0.0	6.043	0.0	0.0
50		5.91	0.412	5.861	2.904	0.111
100		5.79	0.867	5.730	2.626	0.200
150		5.69	1.243	5.622	2.410	0.273
200		5.59	1.562	5.530	2.237	0.335
300	0.90	5.42	2.082	5.379	1.977	0.436
400	1.28	5.28	2.493	5.259	1.790	0.516
500	1.67	5.16	2.832	5.160	1.647	0.583
600	2.00	5.07	3.119	5.077	1.535	0.639
800	2.60	4.91	3.586	4.970	1.367	0.731
1000	3.06	4.78	3.956	4.831	1.246	0.804
1200	3.47	4.67	4.260	4.742	1.155	0.863
1400	3.83	4.57	4.517	4.666	1.082	0.914
1600	4.16	4.49	4.738	4.601	1.038	0.958
1800	4.55	4.42	5.110	4.481		1.036
2000	4.84	4.37	5.269	4.444		1.063

Run 26

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.043 \times 10^{-7}$

$[H_2O] = 2.362 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.043	0.0	6.043	0.0	0.0
50		5.76	0.850	5.710	3.878	0.209
100	0.33	5.55	1.626	5.488	3.373	0.359
150	0.52	5.34	2.222	5.316	3.014	0.475
200	0.75	5.18	2.706	5.176	2.744	0.569
300	1.21	4.96	3.449	4.961	2.363	0.713
400	1.76	4.79	4.007	4.799	2.105	0.822
500	2.40	4.66	4.448	4.670	1.917	0.909
600	2.96	4.54	4.811	4.564	1.773	0.980
800	3.92	4.35	5.380	4.398	1.565	1.092
1000	4.50	4.20	5.812	4.271	1.421	1.177
1200	4.98	4.18	6.155	4.170	1.316	1.244
1400	5.37	3.97	6.436	4.087	1.273	1.300
1600	5.70	3.88	6.763	3.991	1.134	1.364
1800	6.00	3.80	6.950	3.955	1.149	1.401
2000	6.18	3.72	7.128	3.884	1.051	1.436

Run 27

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.043 \times 10^{-7}$

$[H_2O] = 4.724 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.043	0.0	6.043	0.0	0.0
50		5.45	1.643	5.450	5.026	0.379
100	0.57	5.06	2.868	5.099	4.162	0.615
150	0.92	4.82	3.733	4.851	3.608	0.783
200	1.25	4.65	4.388	4.662	3.219	0.910
300	1.95	4.37	5.337	4.388	2.706	1.094
400	2.58	4.18	6.006	4.194	2.379	1.225
500	3.17	4.04	6.511	4.047	2.151	1.324
600	3.87	3.92	6.911	3.930	1.983	1.402
800	4.88	3.72	7.509	3.755	1.748	1.519
1000	5.70	3.56	7.939	3.630	1.593	1.604
1200	6.45	3.42	8.262	3.516	2.442	1.677
1400	7.23	3.31	8.627	3.427	1.409	1.740
1600	7.80	3.20	8.954	3.332	1.267	1.804
1800	8.18	3.10	9.082	3.294	1.226	1.829
2000	8.42	3.00	9.189	3.263	1.168	1.850

Run 28

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.209 \times 10^{-6}$

$[H_2O] = 1.181 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.209	0.0	1.209	0.0	0.0
50		1.15	0.174	1.146	5.254	0.399
100		1.10	0.313	1.106	4.475	0.670
150	0.11	1.07	0.416	1.076	3.955	0.873
200	0.15	1.04	0.499	1.052	3.580	1.034
300	0.25	1.01	0.624	1.016	3.070	1.279
400	0.36	0.99	0.718	0.988	2.734	1.462
500	0.46	0.97	0.791	0.966	2.493	1.608
600	0.55	0.95	0.852	0.949	2.310	1.728
800	0.70	0.92	0.948	0.920	2.049	1.917
1000	0.83	0.90	1.021	0.899	1.869	2.061
1200	0.93	0.89	1.080	0.882	1.736	2.177
1400	1.01	0.88	1.128	0.867	1.635	2.272
1600	1.07	0.87	1.168	0.851	1.573	2.374
1800	1.12	0.87	1.203	0.845	1.515	2.421
2000	1.14	0.86	1.233	0.836	1.434	2.480

Run 29

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.209 \times 10^{-6}$

$[H_2O] = 2.362 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.209	0.0	1.209	0.0	0.0
50		1.10	0.325	1.098	6.747	0.718
100	0.10	1.04	0.541	1.036	5.489	1.138
150	0.16	0.99	0.690	0.992	4.727	1.428
200	0.23	0.96	0.802	0.960	4.211	1.646
300	0.43	0.92	0.962	0.913	3.546	1.961
400	0.61	0.90	1.076	0.880	3.131	2.184
500	0.76	0.87	1.163	0.854	2.843	2.354
600	0.87	0.85	1.232	0.834	2.631	2.489
800	1.04	0.82	1.335	0.804	2.338	2.693
1000	1.17	0.80	1.410	0.782	2.144	2.840
1200	1.28	0.77	1.466	0.765	2.006	2.952
1400	1.33	0.76	1.511	0.752	1.902	3.041
1600	1.38	0.74	1.546	0.741	1.822	3.111
1800	1.42	0.73	1.576	0.733	1.763	3.169
2000	1.44	0.72	1.599	0.726	1.710	3.217

Run 30

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.209 \times 10^{-6}$

$[H_2O] = 4.724 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.209	0.0	1.209	0.0	0.0
50		1.02	0.574	1.020	8.326	1.231
100	0.14	0.93	0.878	0.933	6.439	1.820
150	0.23	0.87	1.068	0.878	5.413	2.190
200	0.32	0.83	1.202	0.839	4.759	2.450
300	0.60	0.78	1.383	0.786	3.966	2.805
400	0.89	0.76	1.502	0.751	3.498	3.040
500	1.08	0.73	1.588	0.726	3.187	3.209
600	1.22	0.71	1.653	0.707	2.967	3.336
800	1.40	0.68	1.745	0.680	2.675	3.516
1000	1.54	0.66	1.805	0.662	2.495	3.636
1200	1.63	0.65	1.848	0.650	2.374	3.719
1400	1.71	0.63	1.878	0.641	2.290	3.779
1600	1.77	0.62	1.900	0.634	2.230	3.833
1800	1.81	0.61	1.917	0.630	2.186	3.856
2000	1.84	0.60	1.929	0.626	2.153	3.880

Run 31

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.813 \times 10^{-6}$

$[H_2O] = 1.181 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.813	0.0	1.813	0.0	0.0
50		1.69	0.373	1.687	7.229	0.818
100	0.20	1.60	0.624	1.614	5.932	1.308
150	0.31	1.554	0.801	1.562	5.142	1.654
200	0.42	1.52	0.936	1.523	4.604	1.918
300	0.65	1.47	1.134	1.465	3.906	2.308
400	0.89	1.42	1.278	1.423	3.465	2.591
500	1.06	1.38	1.390	1.390	3.157	2.811
600	1.21	1.351	1.480	1.363	2.927	2.989
800	1.44	1.30	1.619	1.322	2.605	3.264
1000	1.59	1.26	1.722	1.292	2.388	3.469
1200	1.70	1.23	1.803	1.268	2.232	3.629
1400	1.79	1.20	1.868	1.248	2.113	3.758
1600	1.84	1.18	1.922	1.232	2.020	3.864
1800	1.88	1.16	1.966	1.219	1.945	3.952
2000	1.90	1.50	2.004	1.208	1.884	4.027

Run 32

Initial Conditions:

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.813 \times 10^{-6}$

$[H_2O] = 2.362 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.813	0.0	1.813	0.0	0.0
50		1.63	0.667	1.595	9.041	1.424
100	0.33	1.50	1.035	1.488	7.090	2.140
150	0.53	1.42	1.272	1.419	6.013	2.604
200	0.71	1.37	1.444	1.369	5.318	2.940
300	1.04	1.29	1.683	1.299	4.462	3.410
400	1.29	1.25	1.846	1.251	3.946	3.733
500	1.46	1.22	1.968	1.216	3.599	3.971
600	1.57	1.19	2.062	1.188	3.347	4.157
800	1.76	1.15	2.198	1.147	3.008	4.427
1000	1.91	1.11	2.294	1.119	2.791	4.615
1200	2.03	1.09	2.363	1.099	2.641	4.752
1400	2.13	1.07	2.415	1.084	2.533	4.833
1600	2.19	1.06	2.455	1.072	2.453	4.934
1800	2.23	1.04	2.486	1.062	2.392	5.000
2000	2.26	1.03	2.510	1.055	2.345	5.044

Run 33

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 5.948 \times 10^{-7}$

$[H_2O] = 1.162 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^8$
0	0.0	5.948	0.0	5.948	0.0	0.0
50		5.79	0.385	5.777	2.800	1.049
100		5.65	0.802	5.658	2.500	1.853
150	0.35	5.55	1.139	5.561	2.276	2.506
200	0.52	5.48	1.422	5.480	2.103	3.053
300	0.93	5.36	1.875	5.348	1.849	3.955
400	1.31	5.26	2.231	5.245	1.670	4.630
500	1.62	5.18	2.523	5.160	1.537	5.200
600	1.88	5.10	2.770	5.088	1.432	5.683
800	2.32	4.99	3.170	4.971	1.278	6.468
1000	2.65	4.90	3.487	4.879	1.169	7.090
1200	2.94	4.83	3.747	4.802	1.087	7.602
1400	3.18	4.78	3.966	4.738	1.022	8.305
1600	3.38	4.74	4.156	4.682	0.967	8.409
1800	3.53	4.70	4.419	4.604	0.901	8.928
2000	3.61	4.67	4.554	4.564	0.868	9.196

Run 34

Initial Conditions:

Reactor Temperature: $45.0^{o}C$

Concentrations of Reactants (moles per liter):

$[NO_2] = 5.948 \times 10^{-7}$

$[H_2O] = 2.325 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^{8}$	$\times 10^{7}$	$\times 10^{8}$	$\times 10^{7}$	$\times 10^{9}$	$\times 10^{7}$
0	0.0	5.948	0.0	5.948	0.0	0.0
50		5.65	0.791	5.636	3.718	0.196
100	0.3	5.43	1.494	5.436	3.196	0.331
150	0.5	5.27	2.026	5.284	2.839	0.434
200	0.8	5.15	2.449	5.162	2.578	0.516
300	1.8	4.97	3.097	4.974	2.218	0.642
400	2.4	4.84	3.580	4.834	1.978	0.736
500	2.9	4.73	3.963	4.723	1.806	0.811
600	3.3	4.62	4.276	4.632	1.675	0.872
800	4.2	4.46	4.767	4.488	1.488	0.968
1000	4.5	4.34	5.140	4.379	1.359	1.042
1200	4.9	4.24	5.435	4.292	1.264	1.100
1400	5.2	4.17	5.675	4.219	1.297	1.148
1600	5.5	4.11	5.890	4.158	1.131	1.189
1800	5.7	4.06	6.059	4.108	1.134	1.223
2000	5.8	4.01	6.241	4.055	1.037	1.259

Run 35

Initial Conditions:

Reactor Temperature: $45.0^{o}C$

Concentrations of Reactants (moles per liter):

$[NO_2] = 5.948 \times 10^{-7}$

$[H_2O] = 4.650 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	5.948	0.0	5.948	0.0	0.0
50		5.39	1.523	5.395	4.799	0.353
100	0.55	5.03	2.624	5.082	3.939	0.564
150	0.83	4.83	3.389	4.863	3.407	0.712
200	1.12	4.69	3.964	4.698	3.042	0.823
300	1.76	4.47	4.795	4.458	2.568	0.985
400	2.30	4.30	5.379	4.289	2.271	1.098
500	2.77	4.16	5.820	4.161	2.065	1.185
600	3.19	4.06	6.169	4.059	1.914	1.253
800	3.95	3.88	6.688	3.908	1.705	1.355
1000	4.60	3.74	7.058	3.799	1.568	1.427
1200	5.17	3.64	7.338	3.717	1.471	1.482
1400	5.67	3.56	7.556	3.653	1.398	1.525
1600	6.13	3.50	7.727	3.603	1.342	1.559
1800	6.52	3.45	7.861	3.543		1.596
2000	6.85	3.41	7.975	3.530		1.608

Run 36

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.190 \times 10^{-6}$

$[H_2O] = 1.162 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.190	0.0	1.190	0.0	0.0
50		1.13	0.160	1.132	5.001	0.371
100	0.11	1.09	0.284	1.096	4.206	0.611
150	0.19	1.07	0.375	1.070	3.698	0.788
200	0.27	1.05	0.446	1.049	3.342	0.926
300	0.41	1.02	0.554	1.018	2.866	1.137
400	0.51	1.00	0.634	0.994	2.558	1.294
500	0.59	0.98	0.698	0.976	2.339	1.419
600	0.65	0.97	0.750	0.961	2.174	1.521
800	0.76	0.95	0.831	0.937	1.940	1.682
1000	0.84	0.93	0.894	0.918	1.779	1.805
1200	0.89	0.91	0.943	0.904	1.658	1.904
1400	0.94	0.90	0.984	0.892	1.572	1.984
1600	0.97	0.90	1.018	0.882	1.501	2.051
1800	0.99	0.89	1.047	0.873	1.443	2.109
2000	0.99	0.88	1.072	0.866	1.394	2.158

Run 37

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.190 \times 10^{-6}$

$[H_2O] = 2.325 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.190	0.0	1.190	0.0	0.0
50		1.10	0.299	1.088	6.394	0.662
100		1.04	0.490	1.033	5.157	1.032
150	0.11	0.99	0.620	0.995	4.437	1.284
200	0.16	0.97	0.716	0.967	3.958	1.473
300	0.29	0.93	0.856	0.926	3.350	1.745
400	0.44	0.91	0.959	0.898	2.976	1.938
500	0.57	0.89	1.028	0.876	2.718	2.084
600	0.68	0.87	1.087	0.859	2.529	2.200
800	0.81	0.84	1.176	0.833	2.269	2.374
1000	0.91	0.82	1.239	0.814	2.099	2.500
1200	0.99	0.80	1.287	0.800	1.979	2.594
1400	1.07	0.79	1.324	0.789	1.891	2.667
1600	1.12	0.78	1.353	0.780	1.764	2.724
1800	1.15	0.77	1.377	0.773	1.770	2.771
2000	1.15	0.76	1.396	0.768	1.729	2.809

Run 38

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.190 \times 10^{-6}$

$[H_2O] = 4.650 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.190	0.0	1.190	0.0	0.0
50		1.03	0.525	1.017	7.880	1.129
100	0.10	0.94	0.793	0.940	6.085	1.647
150	0.17	0.88	0.959	0.892	5.137	1.970
200	0.29	0.85	1.076	0.858	4.543	2.198
300	0.56	0.81	1.234	0.812	3.828	2.507
400	0.86	0.78	1.338	0.782	3.411	2.710
500	1.06	0.76	1.412	0.760	3.136	2.856
600	1.18	0.75	1.468	0.744	2.943	2.965
800	1.31	0.72	1.544	0.721	2.691	3.116
1000	1.40	0.70	1.594	0.707	2.539	3.214
1200	1.45	0.69	1.628	0.697	2.440	3.280
1400	1.48	0.68	1.651	0.690	2.373	3.326
1600	1.50	0.67	1.668	0.685	2.327	3.359
1800	1.51	0.66	1.680	0.681	2.294	3.382
2000	1.53	0.66	1.688	0.679	2.270	3.399

Run 39

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.784 \times 10^{-6}$

$[H_2O] = 1.162 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.784	0.0	1.784	0.0	0.0
50		1.66	0.342	1.668	6.827	0.751
100	0.10	1.60	0.562	1.604	5.546	1.180
150	0.19	1.55	0.715	1.560	4.797	1.478
200	0.34	1.52	0.831	1.526	4.297	1.704
300	0.59	1.48	1.001	1.476	3.658	2.038
400	0.81	1.45	1.124	1.440	3.260	2.280
500	0.95	1.42	1.219	1.412	2.983	2.468
600	1.07	1.40	1.296	1.390	2.778	2.619
800	1.25	1.36	1.414	1.355	2.492	2.853
1000	1.38	1.32	1.502	1.329	2.301	3.026
1200	1.47	1.30	1.570	1.309	2.164	3.161
1400	1.53	1.28	1.624	1.293	2.061	3.268
1600	1.56	1.26	1.668	1.279	1.981	3.355
1800	1.58	1.26	1.704	1.269	1.918	3.428
2000	1.61	1.24	1.743	1.260	1.865	3.488

Run 40

Initial Conditions:

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.784 \times 10^{-6}$

$[H_2O] = 2.325 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.784	0.0	1.784	0.0	0.0
50		1.62	0.608	1.585	8.516	1.300
100	0.10	1.59	0.929	1.492	6.653	1.924
150	0.18	1.42	1.134	1.432	5.657	2.323
200	0.29	1.37	1.282	1.389	5.024	2.615
300	0.63	1.30	1.489	1.329	4.253	3.021
400	0.93	1.27	1.630	1.287	3.792	3.298
500	1.14	1.24	1.734	1.257	3.484	3.502
600	1.33	1.22	1.814	1.233	3.263	3.660
800	1.62	1.19	1.929	1.199	2.967	3.888
1000	1.73	1.17	2.008	1.176	2.780	4.044
1200	1.84	1.14	2.064	1.160	2.654	4.154
1400	1.91	1.13	2.105	1.147	2.565	4.236
1600	1.96	1.13	2.105	1.147	2.565	4.236
1800	1.98	1.12	2.159	1.131	2.452	4.345
2000	2.00	1.12	2.177	1.126	2.416	4.378

Run 45

Initial Conditions:

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.171 \times 10^{-6}$

$[H_2O] = 2.289 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

	Concentrations (moles per liter)					
	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0	1.171	0.0	1.171	0.0	0.0
50		1.08	0.266	1.079	6.014	0.596
100	0.14	1.02	0.434	1.031	4.842	0.916
150	0.23	0.99	0.547	0.999	4.173	1.135
200	0.32	0.97	0.631	0.974	3.734	1.299
300	0.49	0.94	0.752	0.939	3.181	1.536
400	0.62	0.91	0.838	0.914	2.842	1.703
500	0.73	0.89	0.902	0.895	2.611	1.830
600	0.81	0.88	0.953	0.880	2.442	1.930
800	0.92	0.85	1.029	0.858	2.211	2.080
1000	0.99	0.83	1.083	0.842	2.062	2.186
1200	1.06	0.82	1.122	0.830	1.958	2.264
1400	1.11	0.81	1.153	0.821	1.882	2.324
1600	1.15	0.81	1.176	0.814	1.825	2.371
1800	1.18	0.81	1.195	0.809	1.782	2.408
2000	1.20	0.81	1.210	0.804	1.748	2.437

Run 46

Initial Conditions:

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.171 \times 10^{-6}$

$[H_2O] = 4.578 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.171	0.0	1.171	0.0	0.0
50		1.02	0.468	1.016	7.434	1.010
100		0.95	0.704	0.948	5.764	1.466
150		0.91	0.850	0.906	4.897	1.749
200	0.10	0.87	0.953	0.876	4.357	1.949
300	0.20	0.83	1.091	0.836	3.714	2.220
400	0.40	0.81	1.182	0.810	3.341	2.397
500	0.67	0.80	1.246	0.791	3.098	2.522
600	0.83	0.78	1.293	0.777	2.929	2.615
800	1.03	0.76	1.357	0.758	2.713	2.713
1000	1.15	0.75	1.397	0.747	2.586	2.820
1200	1.21	0.74	1.423	0.739	2.506	2.871
1400	1.25	0.73	1.440	0.734	2.454	2.906
1600	1.28	0.72	1.452	0.730	2.419	2.928
1800	1.30	0.72	1.460	0.728	2.396	2.944
2000	1.32	0.72	1.466	0.726	2.380	2.955

Run 47

Initial Conditions:

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.757 \times 10^{-6}$

$[H_2O] = 1.144 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.757	0.0	1.757	0.0	0.0
50		1.66	0.304	1.653	6.407	0.671
100		1.59	0.496	1.598	5.185	1.044
150	0.10	1.55	0.628	1.560	4.488	1.302
200	0.14	1.52	0.728	1.530	4.028	1.497
300	0.26	1.48	0.875	1.488	3.446	1.785
400	0.43	1.45	0.981	1.456	3.085	1.994
500	0.60	1.43	1.063	1.432	2.836	2.155
600	0.74	1.41	1.129	1.413	2.652	2.285
800	0.96	1.38	1.230	1.383	2.397	2.485
1000	1.09	1.36	1.304	1.361	2.228	2.631
1200	1.18	1.35	1.361	1.344	2.107	2.744
1400	1.24	1.34	1.406	1.331	2.018	2.833
1600	1.28	1.33	1.442	1.320	1.949	2.904
1800	1.32	1.33	1.472	1.312	1.894	2.962
2000	1.35	1.33	1.496	1.304	1.851	3.010

Run 48

Initial Conditions:

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.757 \times 10^{-6}$

$[H_2O] = 2.289 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^6$	$\times 10^9$	$\times 10^7$
0	0.0	1.757	0.0	1.757	0.0	0.0
50		1.58	0.540	1.579	8.001	1.159
100	0.12	1.48	0.820	1.498	6.261	1.704
150	0.20	1.43	0.999	1.446	5.348	1.205
200	0.31	1.40	1.129	1.409	4.772	2.305
300	0.58	1.36	1.308	1.356	4.076	2.657
400	0.84	1.33	1.430	1.321	3.664	2.897
500	1.04	1.30	1.519	1.294	3.390	3.072
600	1.17	1.28	1.587	1.274	3.194	3.207
800	1.36	1.26	1.684	1.246	2.937	3.398
1000	1.49	1.24	1.748	1.227	2.778	3.525
1200	1.58	1.22	1.793	1.214	2.673	3.613
1400	1.63	1.22	1.825	1.204	2.601	3.676
1600	1.66	1.21	1.848	1.198	2.550	3.721
1800	1.68	1.21	1.865	1.193	2.513	3.754
2000	1.70	1.21	1.877	1.189	2.486	3.779

Run 49

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 1.360 \times 10^{-3}$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.347	0.0	6.347	0.0	0.0
50		6.10	0.576	6.106	3.391	0.149
100		5.92	1.208	5.922	3.116	0.273
150		5.76	1.746	5.765	2.890	0.378
200		5.62	2.211	5.630	2.702	0.469
300		5.38	2.982	5.404	2.404	0.620
400		5.18	3.600	5.224	2.179	0.742
500		5.01	4.111	5.074	2.002	0.842
600		4.87	4.545	4.946	1.859	0.928
800		4.64	5.248	4.739	1.641	1.066
1000		4.45	5.801	4.576	1.482	1.176
1200		4.29	6.252	4.443	1.360	1.265
1400		4.16	6.631	4.331	1.263	1.340
1600		4.05	6.956	4.235	1.184	1.405
1800		3.96	7.238	4.151	1.118	1.461
2000		3.90	7.487	4.077	1.062	1.510

Run 50

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 2.481 \times 10^{-4}$

$[O_2] = 1.360 \times 10^{-3}$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	[NO]	$[NO_2]$	[NO]	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^9$	$\times 10^7$
0	0.0	6.347	0.0	6.347	0.0	0.0
50		5.89	1.178	5.903	4.542	0.281
100		5.59	2.262	5.588	4.005	0.492
150		5.33	3.118	5.340	3.600	0.660
200		5.15	3.816	5.136	3.282	0.796
300		4.84	4.899	4.821	2.816	1.008
400		4.61	5.710	4.584	2.489	1.167
500		4.41	6.349	4.397	2.246	1.293
600		4.24	6.871	4.244	2.057	1.395
800		3.96	7.679	4.007	1.782	1.555
1000		3.74	8.286	3.828	1.591	1.675
1200		3.57	8.765	3.687	1.449	1.770
1400		3.43	9.154	3.571	1.339	1.847
1600		3.31	9.479	3.571	1.339	1.912
1800		3.29	9.755	3.393	1.179	1.967
2000		3.08	9.994	3.322	1.119	2.015

Run 51

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 4.962 \times 10^{-4}$

$[O_2] = 1.360 \times 10^{-3}$

$[NO] = 0.0$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^9$	$\times 10^8$
0	0.0	6.347	0.0	6.347	0.0	0.0
50		5.60	0.226	5.552	5.877	0.510
100		5.01	0.396	5.061	4.893	0.841
150		4.77	0.518	4.710	4.227	1.077
200		4.55	0.609	4.444	3.745	1.256
300		4.07	0.742	4.060	3.093	1.514
400		3.79	0.833	3.793	2.670	1.694
500		3.59	0.902	3.593	2.372	1.829
600		3.42	0.956	3.436	2.151	1.934
800		3.17	1.035	3.202	1.842	2.091
1000		2.97	1.092	3.035	1.636	2.204
1200		2.82	1.135	2.908	1.488	2.289
1400		2.70	1.169	2.807	1.376	2.357
1600		2.59	1.196	2.726	1.289	2.412
1800		2.50	1.219	2.658	1.219	2.458
2000		2.42	1.238	2.601	1.162	2.496

Run 52

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 6.347 \times 10^{-7}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 2.127 \times 10^{-5}$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^5$	$\times 10^7$	$\times 10^5$	$\times 10^7$	$\times 10^9$	$\times 10^8$
0	2.127	6.347	2.127	6.347	0.0	0.0
50		6.20	2.127	6.101	8.358	1.359
100		6.08	2.128	5.960	8.104	2.309
150		5.98	2.128	5.859	7.923	2.988
200		5.90	2.128	5.786	7.793	3.479
300		5.78	2.129	5.693	7.682	4.104
400		5.68	2.129	5.642	7.538	4.447
500		5.64	2.129	5.614	7.488	4.638
600		5.61	2.129	5.598	7.460	4.745
800		5.58	2.129	5.584	7.435	4.840
1000		5.58	2.129	5.579	7.427	4.870
1200						
1400						
1600						
1800						
2000						

Run 53

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.269 \times 10^{-6}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 2.127 \times 10^{-5}$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^5$	$\times 10^6$	$\times 10^5$	$\times 10^6$	$\times 10^8$	$\times 10^7$
0	2.127	1.269	2.127	1.269	0.0	0.0
50		1.21	2.129	1.189	1.220	0.493
100		1.18	2.130	1.146	1.150	0.780
150		1.16	2.131	1.120	1.108	0.958
200		1.14	2.132	1.103	1.081	1.072
300		1.12	2.132	1.084	1.052	1.195
400		1.10	2.133	1.076	1.040	1.250
500		1.09	2.133	1.073	1.034	1.275
600		1.08	2.133	1.071	1.031	1.286
800		1.07	2.133	1.070	1.029	1.294
1000		1.07	2.133	1.070	1.029	1.295
1200						
1400						
1600						
1800						
2000						

Run 54

Initial Conditions:

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO_2] = 1.842 \times 10^{-6}$

$[H_2O] = 1.240 \times 10^{-4}$

$[O_2] = 0.0$

$[NO] = 2.127 \times 10^{-5}$

Concentrations (moles per liter)

	Experimental		Predicted			
Time	$[NO]$	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$	$[HNO_3]$
(min)	$\times 10^5$	$\times 10^6$	$\times 10^5$	$\times 10^6$	$\times 10^8$	$\times 10^7$
0	2.127	1.842	2.127	1.842	0.0	0.0
50		1.73	2.131	1.690	1.496	0.963
100		1.68	2.134	1.616	1.382	1.457
150		1.64	2.135	1.575	1.319	1.736
200		1.62	2.136	1.550	1.283	1.901
300		1.59	2.137	1.526	1.247	2.065
400		1.57	2.137	1.516	1.233	2.129
500		1.55	2.137	1.513	1.228	2.154
600		1.54	2.137	1.511	1.225	2.165
800		1.52	2.137	1.510	1.224	2.171
1000		1.50	2.137	1.510	1.224	2.172
1200						
1400						
1600						
1800						
2000						

Appendix E. Numerical Solution to Chemical Rate Equations

APPENDIX E. NUMERICAL SOLUTION TO CHEMICAL RATE EQUATIONS

Summary

The numerical solution of the rate equations encountered in the gas-phase reaction of nitrogen dioxide with water vapor is described.

Discussion

If the rate equations for each species in a reacting system are known, the system can be completely described as a function of time. In general, this system of equations can be solved numerically. No simplifications such as the steady-state hypothesis need be made.

The rate of reaction of nitrogen dioxide with water vapor is controlled by the following overall reaction:

$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad . \qquad (A)$$

By the law of mass action, the rate of production of nitrogen dioxide is,

$$R_{NO_2} = -2k_A(NO_2)^2(H_2O) + 2k_A'(HNO_2)(HNO_3) \quad ,$$

or

$$R_{NO_2} = -2k_A(NO_2)^2(H_2O) + 2(k_A/K_A)(HNO_2)(HNO_3) \quad . \qquad (1)$$

Nitrous acid decomposes by the reaction,

$$2HNO_2 = NO + NO_2 + H_2O \quad . \qquad (B)$$

Equation (1) must be modified to include the production of nitrogen dioxide according to reaction (B):

$$R_{NO_2} = -2k_A(NO_2)^2(H_2O) + 2(k_A/K_A)(HNO_2)(HNO_3) + k_B(HNO_2)^2 - (k_B/K_B)(NO)(NO_2)(H_2O) \quad . \quad (2)$$

Equation (2) takes into account a finite rate for reaction (b), even though the reaction is essentially at equilibrium. The four independent equations which describe the reacting system are,

$$R_{NO_2} = -2k_A(NO_2)^2(H_2O) + 2(k_A/K_A)(HNO_2)(HNO_3) + k_B(HNO_2)^2 - (k_B/K_B)(NO)(NO_2)(H_2O) \quad . \quad (2)$$

$$R_{HNO_3} = k_A(NO_2)^2(H_2O) - (k_A/K_A)(HNO_2)(HNO_3) \quad . \quad (3)$$

$$R_{HNO_2} = -2k_B(HNO_2)^2 + 2(k_B/K_B)(NO)(NO_2)(H_2O) + k_A(NO_2)^2(H_2O) - (k_A/K_A)(HNO_2)(HNO_3) \quad . \quad (4)$$

$$R_{NO} = k_B(HNO_2)^2 - (k_B/K_B)(NO)(NO_2)(H_2O) \quad . \quad (5)$$

Numerical integration began from the initial conditions, normally,

$$(NO_2)_o = (NO_2)_o$$

$$(NO)_o = 0.0$$

$$(HNO_3)_o = 0.0$$

$$(HNO_2)_o = 0.0 \quad .$$

The solutions obtained from the integration of equations (2) through (5) were checked by a material balance on fixed nitrogen:

$$(NO_2)_o = (NO_2) + (NO) + (HNO_2) + (HNO_3) \quad . \qquad (6)$$

The integration was performed on an IBM 360/75 digital computer with the DEQ subroutine. The subroutine uses the method of Runge-Kutta-Gill to start the integration, and the Adams-Moulton method to continue. A one-second interval was used in the variable-step mode of the subroutine. Error was set at one part-per-million.

Agreement of the solutions with experimental data was found by varying the values of k_A and K_A for runs at 25°C. A rough estimate of k_A could be made from the raw data. At other temperatures, only k_A was changed arbitrarily. The value of K_A was determined from the calculations of Forsythe and Giauque[14], and the value of K_A at 25°C.

For comparison of runs when oxygen was present as a primary reactant, account was taken of the reaction,

$$2NO + O_2 = 2NO_2 \quad . \qquad (C)$$

The rate of formation of nitrogen dioxide was then,

$$R_{NO_2} = -2k_A(NO_2)^2(H_2O) + 2(k_A/K_A)(HNO_2)(HNO_3) + k_B(HNO_2)^2 - (k_B/K_B)(NO)(NO_2)(H_2O) + k_C(NO)^2(O_2) \quad .$$

The rate of formation of nitric oxide was,

$$R_{NO} = k_B(HNO_2)^2 - (k_B/K_B)(NO)(NO_2)(H_2O) - k_C(NO)^2(O_2) \quad .$$

The equations were integrated as before. The concentration of oxygen was taken as constant.

Part II

The Rate and Mechanism of the Air Oxidation of Parts-Per-Million Concentrations of Nitric Oxide in the Presence of Water Vapor

I. INTRODUCTION

The influence of the oxides of nitrogen in air pollution is a subject of increasing interest. Nitric oxide and nitrogen dioxide, produced from the burning of fuels in air, initiate a complex series of reactions which results in photochemical smog. One of the important reactions occurring in air is the conversion of nitric oxide to nitrogen dioxide:

$$2NO + O_2 = 2NO_2 \quad . \qquad (A)$$

This reaction has been widely studied. Although much of the current interest has been centered on the reaction in dry air[2,8,9,16], most of the work has been centered on the role of the reaction in the production of nitric acid. The reaction also has considerable scientific interest in that it follows third-order kinetics.

In industrial operations, the oxidation seldom proceeds as a simple combination of nitric oxide and oxygen. Rather, it occurs as part of an overall system designed to produce nitric acid. Nitric oxide, oxygen, nitrogen dioxide, water and nitrogen occur together as gas-phase reactants in the common industrial process. The kinetics of this system have been studied, but mostly with reference to the rate of the formation of aqueous nitric acid. The gas-phase reactions have not been studied in detail, and the complete mechanism of the production of nitric acid is not known.

In particular, the role of water as a primary reactant in the gas-phase system is not known. Studies on the effect of water vapor on the oxidation of nitric oxide are conflicting. Some investigators have reported that water vapor has no effect on the oxidation[9,21]. Others have found that water vapor may increase or decrease the rate of oxidation[7,12,17,19]. Earlier studies, presented in Part I of this thesis, showed that nitrogen dioxide was consumed in the gas phase by water vapor. Thus, the production of nitrogen dioxide from the oxidation of nitric oxide should be lowered by the presence of water vapor.

In view of the conflicting evidence concerning the role of water in the thermal oxidation of nitric oxide, a study was undertaken to determine the kinetics and mechanism of the reactions involved in the wet oxidation. The object of the experiment was to obtain the concentrations of each substance present during the wet oxidation as a function of time. From these data, the rate of reaction, the mechanism of the reaction, and the product distribution could be determined. The primary purpose of the study was to enable the prediction of the concentrations of each component as a function of time for any similar system.

II. LITERATURE

In a gas-phase mixture of nitric oxide, oxygen, nitrogen dioxide and water vapor, three known reactions occur. These are (1) the oxidation of nitric oxide,

$$2NO + O_2 = 2NO_2 \quad , \qquad (A)$$

(2) the formation of nitrous acid vapor,

$$NO + NO_2 + H_2O = 2HNO_2 \quad , \qquad (B)$$

and (3) the formation of nitric acid vapor,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (C)$$

An understanding of the kinetics of each reaction is needed to determine the influence of water vapor on the rate of oxidation of nitric oxide.

A. The Oxidation of Nitric Oxide

The reaction of oxygen with nitric oxide has been widely studied. The complete mechanism is subject to controversy. The overall reaction,

$$2NO + O_2 = 2NO_2 \quad , \qquad (A)$$

initially follows third-order kinetics according to the equation

$$R_{NO} = -k_A(NO)^2(O_2) \quad ,$$

where R represents the rate of production of nitric oxide. The value of the third-order rate constant, k_A, is about

1.5×10^4 liter^2 mole^{-2} sec^{-1} at 25°C. This value decreases with increasing temperature. Trotman-Dickenson[22] correlated the results of several studies, and obtained an overall activation energy for reaction (A) of -1.5 kilocalories.

Several studies of the oxidation have been made with particular reference to the termolecular nature of the reaction. Glasson and Tuesday[8] studied the oxidation in dry air using long-path infrared spectroscopy. The absorption of nitrogen dioxide was measured at 1600 cm^{-1}. The initial concentration of nitric oxide was varied from one to 40 ppm. They determined a value of 1.54×10^4 liter^2 mole^{-2} sec^{-1} for the third-order rate constant at 23°C. No deviations from third-order behavior were reported. Greig and Hall[9] used a similar spectroscopic method to study the oxidation. They measured the concentration of nitric oxide at 1905 cm^{-1}. The value of the third-order rate constant was 2.0×10^4 liter^2 mole^{-2} sec^{-1} at 20°C. They also found no deviations from third-order kinetics. The activation energy for reaction (A) was -0.95 kilocalories.

Treacy and Daniels[21] studied the oxidation of nitric oxide at low total pressures from one to 20 mm Hg. The concentration of nitrogen dioxide was measured photometrically. They reported that, initially the reaction rate was slightly greater than second order with respect to nitric oxide, and was first order with respect to oxygen. As the pressure of

nitric oxide increased, the reaction followed third-order behavior more closely. The presence of nitrogen dioxide decreased the rate slightly.

Solc[18] repeated the studies of Treacy and Daniels and observed similar behavior. The total pressure was below 70 mm Hg. The initial partial pressure of nitric oxide was varied from one to 50 mm Hg. Solc reported that the third-order rate constant decreased as the ratio of oxygen to nitric oxide increased. The limiting value of the rate constant was 1.48×10^4 liter^2 mole^{-2} sec^{-1} at 25°C. Solc suggested that the reaction took place in the low-pressure region where energy transfer limited the rate of reaction. He proposed the following mechanism for the oxidation:

$$NO + NO = N_2O_2^* \qquad (a)$$

$$N_2O_2^* + O_2 = N_2O_2 + O_2 \qquad (b)$$

$$N_2O_2^* + NO = N_2O_2 + NO \qquad (c)$$

$$N_2O_2 + O_2 = 2NO_2 \qquad (d)$$

$$N_2O_2^* + O_2 = 2NO_2 \quad . \qquad (e)$$

Reactions (b) and (c), involving only energy transfer, would limit the rate at low pressures.

Guillory[10] studied the oxidation of nitric oxide using long-path infrared spectroscopy to measure the concentration of nitric oxide. The pressure of nitric oxide was varied from one to three mm Hg. He reported that, initially, the

reaction followed third-order kinetics. As the pressure of nitric oxide decreased, the order of the reaction with respect to nitric oxide decreased towards unity. Guillory proposed the following mechanism for the oxidation:

$$NO + O_2 = OONO \qquad \text{(fast)}$$

$$OONO + NO = 2NO_2 \quad . \qquad \text{(slow)}$$

The first reaction may become rate-limiting at lower pressures of nitric oxide. Guillory reported spectroscopic evidence of the peroxy-nitrogen trioxide intermediate, OONO[23].

Morrison, Rinker and Corcoran[16] studied the oxidation of nitric oxide in dry air, using gas chromatography to analyze for nitrogen dioxide. The initial concentration of nitric oxide was varied from two to 75 ppm. They reported that the reaction initially followed third-order kinetics. In addition, the presence of nitrogen dioxide increased the rate, following the equation

$$R_{NO} = -k_1(NO)^2(O_2) \; -k_2(NO)(NO_2)(O_2) \quad .$$

The values of k_1 and k_2 were 1.313×10^4 and 1.276×10^4 liter^2 mole^{-2} sec^{-1}, respectively, at 26.5°C.

In all of the previous studies, the initial rate of oxidation of nitric oxide was second order with respect to nitric oxide, and first order with respect to oxygen. Various mechanisms were proposed to explain experimental devi-

ations from this behavior. In the present work, the emphasis was to establish precisely the kinetics of this reaction over a narrow range of temperature and concentration. In a limited range of concentration, the oxidation of nitric oxide can be described by third-order kinetics. Once the third-order rate constant is established experimentally, the role of water on the oxidation can be determined quantitatively by difference from the third-order behavior.

B. The Role of Water in the Oxidation of Nitric Oxide

Evidence on the role of water in the oxidation of nitric oxide is conflicting. Treacy and Daniels[21] found no detectable change in the rate of oxidation when water was present. No deviations from the dry behavior were noted when up to 0.5 mm Hg of water vapor was added to a low-pressure mixture of nitric oxide and oxygen. Greig and Hall[9] reported that, at 20°C, water did not change the rate of oxidation of parts-per-million concentrations of nitric oxide in air. Using long-path infrared spectroscopy, they measured the concentrations of nitric oxide (at 1905 cm^{-1}) and nitrogen dioxide (at 1600 cm^{-1}). Although nitric oxide showed third-order behavior, nitrogen dioxide did not. They suggested that both water and nitric oxide catalyzed surface reactions involving primarily nitrogen dioxide.

Other studies have shown pronounced effects of water on the oxidation. Smith[17] reported that, in the presence

of small amounts of water, the oxidation of nitric oxide began more slowly than in a dry system, and that the reaction appeared to stop short of completion. Monitoring the concentration of nitrogen dioxide photometrically, he found that, in some instances, the amount of nitrogen dioxide began to decrease. Smith found that when his reactor was dried by evacuation during successive determinations, erratic results were obtained. These he attributed to the adsorption of nitric oxide on the reactor surface.

Hasche[12] reported that water catalyzed the oxidation of nitric oxide. At pressures of 91 mm Hg of nitric oxide and 115.5 mm Hg of oxygen, small amounts of water increased the rate of reaction up to 50 percent. The reaction rate was faster in a glass vessel than in a paraffin-coated vessel. Burdick[7] reported that the presence of water decreased the rate of oxidation. He found that, while the rate usually displayed a negative temperature coefficient, the presence of water caused the rate to increase with temperature.

In these studies, water did not change the rate of oxidation appreciably when nitric oxide was present initially at low concentrations. Such was the case in the work of Greig and Hall[9] and of Treacy and Daniels[21]. When the concentration of nitric oxide was higher, water changed the rate appreciably. In addition, the nature of the reactor surface affected the rate. This was found in the studies of

Hasche[12] and Smith[17].

C. The Formation of Nitrous Acid Vapor

When nitric oxide, nitrogen dioxide and water occur together in the gas phase, nitrous acid vapor is formed by the overall reaction

$$NO + NO_2 + H_2O = 2HNO_2 \quad . \qquad (B)$$

The equilibrium of Reaction (B) has been studied by Ashmore and Tyler[3], Karavaev[15], Waldorf and Babb[27], and Wayne and Yost[28]. Their work is summarized in Table 1. Wayne and Yost[28] and Karavaev[15] used the data of Abel and Neusser[1] on the vapor pressure of nitrous acid over aqueous nitrite solutions to calculate the equilibrium constant:

$$K_B = (HNO_2)^2/(NO)(NO_2)(H_2O) \quad .$$

Ashmore and Tyler[3] and Waldorf and Babb[27] measured the equilibrium constant directly. In both studies, the three reactants were mixed with nitric oxide in great excess to retard the formation of nitric acid by the overall reaction

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (C)$$

The concentration of nitrogen dioxide and the total pressure at equilibrium were measured. From these values, the equilibrium constant could be determined. The value of K_B in each of the studies was about 1.5 atm^{-1} at 25°C.

Wayne and Yost[28] studied the kinetics of reaction (B) in a stopped-flow apparatus. They reported that the

reaction was very fast. Leighton[30] described the reaction by third-order kinetics,

$$R_{HNO_2} = 2k_B(NO)(NO_2)(H_2O) - 2k_B'(HNO_2)^2 \quad ,$$

and calculated a value from the data of Wayne and Yost for k_B of 4.3×10^7 liter^2 mole^{-2} sec^{-1} at 25°C. This represents a reaction which is about 3000 times faster than the oxidation of nitric oxide.

The mechanism of reaction (B) is generally thought to include the two bimolecular reactions,

$$NO + NO_2 = N_2O_3 \qquad \text{(fast)} \quad \text{(D)}$$

$$N_2O_3 + H_2O = 2HNO_2 \quad . \qquad \text{(slow)} \quad \text{(E)}$$

The presence of dinitrogen trioxide, N_2O_3, in mixtures of nitrogen dioxide and nitric oxide is well known. Reaction (D) has been studied by Beattie and Bell[4], Bodenstein[5], and Verhoek and Daniels[25]. Hisatsune[13] has calculated the thermodynamic quantities of the sesquioxide as a function of temperature. The value of K_D is 11.9 liter mole^{-1} at 25°C. The second-order rate constant for reaction (D) has been estimated by Vlastaras and Winkler[26] from flow reactor data. They suggested a value of 1.3×10^6 liter mole^{-1} sec^{-1} at 25°C for the value of k_D in the equation

$$R_{NO} = -k_D(NO)(NO_2) \quad .$$

Evidence of the occurrence of reaction (E) comes primarily from the studies on the decomposition of aqueous

solutions of nitrous acid. Turney[23] found that N_2O_3 was extracted by non-polar solvents from aqueous solutions of the acid. Usubillaga[24] reported that the decomposition proceeded by the mechanism,

$$2HNO_2 = N_2O_3 + H_2O$$

$$N_2O_3 = NO + NO_2$$

$$2NO_2 = N_2O_4$$

$$N_2O_4 + H_2O = HNO_2 + HNO_3 \quad .$$

The overall reaction was

$$3HNO_2 = 2NO + HNO_3 + H_2O \quad ,$$

the stoichiometry of which was confirmed by Turney[23]. The mechanism represented by reactions (D) and (E) predicts initial third-order kinetics for reaction (B), viz.,

$$R_{HNO_2} = 2K_D k_E (NO)(NO_2)(H_2O) \quad .$$

No experimental verification of this mechanism has been made.

The gas-phase formation of nitrous acid represents a sink for the fixed nitrogen in nitric oxide and nitrogen dioxide. As a result, water would be expected to lower the concentrations of the oxides during the oxidation of nitric oxide. This effect has been noted only by Smith[17] and Burdick[7]. Greig and Hall[9] may have noted similar behavior in the effects they attributed to surface reactions.

D. The Formation of Nitric Acid Vapor

Nitrogen dioxide and water vapor react in the gas phase to form nitric acid vapor and nitric oxide,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (C)$$

Reaction (C) was studied in Part I of this thesis. The equilibrium constant, calculated from the equation

$$K_C = (NO)(HNO_3)^2/(NO_2)^3(H_2O) \quad ,$$

was equal to 0.137 atm^{-1} at 25°C. Nitric acid vapor is formed by the following overall steps:

$$2NO_2 + H_2O = HNO_2 + HNO_3 \qquad (slow) \qquad (F)$$

$$2HNO_2 = NO + NO_2 + H_2O \quad . \quad (fast) \qquad (G)$$

Reaction (F) controls the rate of reaction, described by the equation

$$R_{HNO_3} = k_F(NO_2)^2(H_2O) - k_F'(HNO_2)(HNO_3) \quad .$$

The value of k_F is 5.50×10^4 $liter^2$ $mole^{-2}$ sec^{-1} at 25°C. In the same units, k_F' is equal to 5.85×10^3 at 25°C.

As with nitrous acid vapor, the formation of nitric acid vapor will consume some of the nitrogen dioxide formed by the oxidation of nitric oxide when water is present.

E. Summary of the Literature

The oxidation of nitric oxide in the presence of water vapor involves the three reactions:

$$2NO + O_2 = 2NO_2 \qquad (A)$$

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (B)$$

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (C)$$

These reactions have been studied separately, but the interactions of the three have not been examined.

The oxidation of nitric oxide is not greatly affected by the presence of water vapor. Only Hasche[12] reported that water vapor increased the rate of oxidation. His work was done with high concentrations of both nitric oxide and oxygen. Treacy and Daniels[21] and Greig and Hall[9] found no appreciable change in the rate at very low concentrations of the reactants. Smith[17] and Burdick[7] found a small decrease in the rate at intermediate concentrations. No great catalytic behavior can be attributed to water vapor.

The kinetics of the formation of nitrous acid vapor are not established. The reaction is unfavorable in the gas phase according to thermodynamics. Since the kinetics of reactions (A) and (C) can be determined separately, it is possible to measure the kinetics of reaction (B) by studying the oxidation of nitric oxide in the presence of water vapor. The direct measurement of the rate cannot be made because of experimental difficulties associated with the high rate of reaction and the limited extent of reaction. These are discussed in the following section.

III. EXPERIMENTAL METHOD

The present study measured the kinetics of the oxidation of nitric oxide, and the kinetics of the oxidation of nitric oxide in the presence of water vapor. The rates of the two reactions were compared, and from these data, the rate of formation of nitrous acid vapor was determined.

The reaction of parts-per-million concentrations of nitric oxide with large excesses of both oxygen and water vapor were examined. As a result, the concentrations of the latter two compounds did not change significantly during the reaction. The reactions took place in the absence of light and at ambient temperature.

The reactants were mixed in a constant-volume batch reactor. Gas-liquid chromatography was used to analyze for the concentration of nitrogen dioxide as a function of time. Nitric oxide could not be determined because of the interference of oxygen in the chromatogram. Samples were withdrawn periodically from the reaction mixture, and were injected into the chromatograph.

The oxidation of nitric oxide was studied to gather preliminary data for the nitric oxide-oxygen-water vapor reaction system. Nitric oxide, oxygen and nitrogen were mixed in the reactor, and the concentration of nitrogen dioxide was monitored as a function of time. The third-order rate constant for the reaction,

$$2NO + O_2 = 2NO_2 \quad , \qquad (A)$$

was determined from 25° to 50°C. Deviations from third-order behavior were sought, although the orders with respect to nitric oxide and oxygen were not studied.

The oxidation of nitric oxide in the presence of water vapor was studied over the same temperature range. Nitric oxide, oxygen, water vapor and nitrogen were mixed in the reactor, and the concentration of nitrogen dioxide was monitored as a function of time. The deviations of this system from the dry oxidation were measured and used to calculate the rate of the reaction,

$$NO + NO_2 + H_2O = 2HNO_2 \quad , \qquad (B)$$

at 40°, 45° and 50°C. No direct measurement of nitrous acid vapor was made. The effect of surface was studied because, at the lower temperatures, the rate of oxidation increased slightly with increasing surface. An accurate measurement of the rate of reaction (B) was not obtainable below 40°C because of these effects.

Interference from the overall reaction,

$$3NO_2 + H_2O = NO + 2HNO_3 \quad , \qquad (C)$$

was prevented by measuring the rate of the wet oxidation only when the concentration of nitrogen dioxide was less than ten ppm. The oxidation was followed for only about 50 minutes. This procedure effectively eliminated reaction (C) as an

influence in the concentration of nitrogen dioxide. In the greatest case encountered, the reaction of water vapor with nitrogen dioxide would consume only about 0.12 ppm of nitrogen dioxide from the oxidation.

The direct measurement of reaction (B) was not made. This was due to difficulties associated with the limited extent of formation of nitrous acid vapor, and to the rapid rate at which the acid vapor is formed. As an example, the reaction would proceed to only one percent completion if 100 ppm of each oxide of nitrogen were allowed to react with 1000 ppm of water vapor. The small change in the concentrations of the oxides of nitrogen would be too small to measure by gas chromatography. In addition, half of the reaction that would occur would take place in the first 700 seconds. The reaction could be slowed by reducing the concentrations of the reactants. For initial concentrations of 10 and 100 ppm of nitrogen dioxide and nitric oxide, respectively, and for 1000 ppm of water vapor, the time for half reaction would be about 800 seconds. The extent of formation of nitrous acid vapor would be less, but in this case, the change in the concentration of nitrogen dioxide would amount to about four percent at equilibrium. The data for these examples are listed in Table 2. As the concentration of nitrogen dioxide decreases, the extent of reaction decreases, but the fractional change in the concentration of nitrogen dioxide increases.

By studying the formation of nitrous acid vapor during the wet oxidation of nitric oxide, it was possible to create a system for short periods where the concentration of nitrogen dioxide was very low, and that of nitric oxide was relatively high. The reaction to form nitrous acid was slow at the beginning of the oxidation when the concentration of nitrogen dioxide was low. The reaction became faster as the oxidation proceeded. By following second-order changes in the concentration of nitrogen dioxide, the rate of formation of nitrous acid vapor could be determined.

IV. EXPERIMENTAL PROCEDURE

An experimental run began by evacuating the reactor to a pressure of less than five microns. The reactor was then pressurized to one atmosphere pressure with dry nitrogen, and evacuated again. This procedure was followed to reduce residual water, nitrogen dioxide, or acid vapors on the reactor surface.

The calibrated mixture of nitric oxide in nitrogen (220 ± 3.5 ppm) was added to the evacuated reactor. Oxygen was added next, always in the amount of 1.00 in. Hg. Timing began at the beginning of this step. Next, wet nitrogen was added. Finally, dry nitrogen was used to pressurize the mixture to 30.00 in. Hg.

Before a run, the chromatograph was conditioned by injecting several standard samples of nitrogen dioxide into the column. Following this, a single standard sample was injected five minutes before the first reactor sample was taken. During this interval, the reaction gases were mixed. At least two samples were drawn through the sampling capillary so that the first sample injected into the chromatograph was an accurate representation of the reaction mixture. The initial sampling was then made. The reaction mixture was analyzed for nitrogen dioxide each 200 seconds.

The chromatograph was calibrated as discussed in Part I, Section IV of this thesis. The final standard sample was used to detect deviations from the calibration curve.

V. EXPERIMENTAL RESULTS

A. Range of Study

The experiment examined the oxidation of nitric oxide, and the oxidation of nitric oxide in the presence of water. From the latter study, the rate of formation of nitrous acid vapor was measured. The reactions were studied from 25° to 50°C. At higher temperatures, the equilibrium concentration of nitrous acid vapor is very low (less than 0.1 ppm at 25°C for the concentrations of reactants used in the present study). The concentration of oxygen in each test was 3.33 percent (1.272×10^{-3} moles liter^{-1} at 25°C).

The dry oxidation was studied with nitric oxide present initially at concentrations of 50.3, 100.6, and 150.9 ppm (2.217×10^{-6}, 4.254×10^{-6}, and 8.508×10^{-6} moles liter^{-1}, respectively, at 25°C) at each temperature. For the wet studies, nitric oxide was present initially at concentrations of 50.3 and 100.6 ppm at each temperature. The initial concentration of water vapor varied from 0.30 to 1.21 percent (1.24×10^{-4} to 4.96×10^{-4} mole liter^{-1} at 25°C). The experimental data are presented in Appendix A. A summary of the initial reaction conditions is included.

B. The Oxidation of Nitric Oxide

Three tests at five-degree intervals from 25° to 50°C were made to determine the third-order rate constants for the reaction,

$$2NO + O_2 = 2NO_2 \quad . \qquad (A)$$

Time-concentration profiles for nitrogen dioxide were obtained, and were plotted on 50-cm graph paper. The profiles were compared graphically to the integrated form of the third-order rate equation,

$$(NO_2) = 1/\ [1/(NO)_o + k_A(O_2)t] \quad , \qquad (1)$$

where $(NO)_o$ is the initial concentration of nitric oxide, and t is the elapsed time of reaction. The value of k_A was varied until the best agreement to the data was found.

The value of k_A was 1.46 ($\pm$ 0.03) x 10^4 liter^2 mole^{-2} sec^{-1} at 25°C. Values at other temperatures are listed in Table 3. The rate of reaction decreased slightly with temperature. Figure 1 shows the data for run 10, taken at 40°C. The concentration of nitrogen dioxide ranged from zero at the beginning of the reaction to 4.8 ppm after 50 minutes.

The value of the third-order rate constant is in good agreement with that found by other investigators. In units of liter^2 mole^{-2} sec^{-1}, the value in the present work was 1.46 at 25°C. Taking into account the negative temperature dependence of the rate constant, this value compares favorably with the studies in air by Morrison (1.30 at 26.5°C), Greig and Hall (2.0 at 20°C), and Glasson and Tuesday (1.54 at 23°C). In addition, Bodenstein[6] and Solc obtained similar values (1.49 and 1.48, respectively at 25°C) at work below 100 mm Hg total pressure. The value found in the

present work differed significantly from the values reported by Altshuller (3.5 at 45°C), and by Treacy and Daniels (0.75 at 25°C).

The reaction was followed only to about 12-percent completion. In this range, no deviation from third-order kinetics was found. The activation energy of the third-order reaction was calculated from the temperature dependence of the rate constant, and from the Arrhenius equation,

$$k_A = k_A^{\circ} \exp(-E_a/RT) \quad .$$

The activation energy was -1.197 ($\pm$ 0.05) kilocalories. This value was greater than that reported by Greig and Hall (-0.95 kcal), but less than those of Trotman-Dickenson (-1.5 kcal) and Tipper and Williams[20] (-1.7 kcal). Figure 2 shows the Arrhenius plot for k_A.

The extent of the reactor surface was not a factor in the oxidation. Figure 3 shows the results of three comparable tests taken on the glass reactor (S/V ratio of 0.355 cm^{-1}), a similar glass reactor containing glass beads (S/V ratio of 1.2 cm^{-1}), and a glass reactor coated with Carbowax 5000, a polyethylene glycol (S/V ratio of 0.355 cm^{-1}). No significant change in the reaction was found.

C. The Oxidation of Nitric Oxide in the Presence of Water

The oxidation of nitric oxide in the presence of water vapor was studied at five-degree intervals from 25° to 50°C. The concentrations of water vapor and oxygen were large compared with those of nitric oxide and nitrogen dioxide.

The reaction was changed by the nature and the extent of the surface available to it. When the wet oxidation took place in the reactor coated with Carbowax 5000 (S/V ratio of 0.355 cm^{-1}), the initial rate of oxidation increased severalfold over that of the dry oxidation (see Figure 4). As the reaction proceeded, the concentration of nitrogen dioxide began to decrease. It was thought that water catalyzed the attack of the oxides of nitrogen on the coating. The effects were not reproducible quantitatively. These effects did not occur in the dry oxidation.

For the uncoated reactors, the rate of oxidation increased with increasing S/V ratio at temperatures below 35°C. Figure 5 compares two runs at 30°C, taken on glass reactors with S/V ratios of 0.355 and 1.2 cm^{-1}. The increased rate was not great, amounting to a 21-percent increase in the concentration of nitrogen dioxide in the greatest case. When the temperature was raised above 35°C, the surface effects disappeared. This was attributed to decreased adsorption of gases on the surface of the reactor.

Above 35°C, the concentration of nitrogen dioxide during the wet oxidation was lower than predicted from the data on the dry oxidation. The difference could not be attributed to surface reactions because the extent of surface had little effect on the reaction at the higher temperatures. In addition, reaction conditions were chosen so that the reaction of water vapor with nitrogen dioxide would not interfere appreciably with the oxidation.

The deviations from dry behavior were attributed to the reaction

$$NO + NO_2 + H_2O = 2HNO_2 \quad . \qquad (B)$$

To determine the rate of this reaction, the data were compared with a rate expression for nitrogen dioxide which represented both the production of nitrogen dioxide by the dry oxidation, and the equilibrium reaction of nitric oxide, nitrogen dioxide and water vapor to form nitrous acid vapor.

The rate of formation of nitrogen dioxide from the oxidation of nitric oxide is described by the equation,

$$R_{NO_2} = d(NO_2)/dt = k_A(NO)^2(O_2) \quad . \qquad (2)$$

The value of k_A was taken from the preliminary studies. The rate of formation of nitrous acid vapor was assumed to follow the kinetics implied by reaction (B). The rate of consumption of nitrogen dioxide by this reaction is

$$R_{NO_2} = -k_B(NO)(NO_2)(H_2O) + k_B'(HNO_2)^2 \quad . \qquad (3)$$

The reverse rate constant, k_B', is related to the forward rate constant by the equilibrium constant for reaction (B) by the equation

$$k_B' = k_B/K_B \quad , \tag{4}$$

where K_B is equal to

$$K_B = (HNO_2)^2/(NO)(NO_2)(H_2O) \quad . \tag{5}$$

Then, the concentration of nitrogen dioxide as a function of time in the wet oxidation is described by the equation,

$$R_{NO_2} = k_A(NO)^2(O_2) - k_B(NO)(NO_2)(H_2O) + (k_B/K_B)(HNO_2)^2 \quad . \tag{6}$$

Equation (6) was solved numerically by digital computer by solving simultaneously the rate equations for nitrous acid vapor and nitric oxide derived from reactions (A) and (B):

$$R_{NO} = -k_A(NO)^2(O_2) - k_B(NO)(NO_2)(H_2O) + (k_B/K_B)(HNO_2)^2 \quad , \tag{7}$$

$$R_{HNO_2} = 2k_B(NO)(NO_2)(H_2O) - 2(k_B/K_B)(HNO_2)^2 \quad . \tag{8}$$

A material balance on fixed nitrogen checked the solution:

$$(NO)_o = (NO) + (NO_2) + (HNO_2) \quad . \tag{9}$$

The experimental data above 35°C were compared to equations (6), (7) and (8) by varying the value of k_B until the experimental and calculated concentration profiles for nitrogen dioxide coincided. The value of the third-order rate constant, k_B, was 1.5 ($\pm$ 0.5) x 10^5 liter^2 mole^{-2} sec^{-1}

at 40°C. The probable error was large because only a second-order change in the concentration of nitrogen dioxide was measured. The value of the rate constant did not change measurably with temperature up to 50°C. Thus, the activation energy for reaction (B) was near zero.

Figures 6, 7 and 8 show the experimental and predicted profiles for nitrogen dioxide for runs at 40°, 45° and 50°C, respectively. The extent of formation of nitrous acid vapor was less at the higher temperatures. The formation of nitric acid vapor was effectively retarded by studying the wet oxidation only when the concentration of nitrogen dioxide was less than 10 ppm. The predicted time-concentration profiles for nitrogen dioxide are in good agreement with the experimental data, especially for the runs at 40°C. The estimated arror for the value of k_B was about 33 percent. At 45° and 50°C, the error is greater, being up to 75 percent at 50°C.

The mechanism of the formation of nitrous acid vapor is generally thought to be described by the reactions,

$$NO + NO_2 = N_2O_3 \qquad \text{(fast)} \qquad \text{(D)}$$

$$N_2O_3 + H_2O = 2HNO_2 \quad \text{(slow)} \qquad \text{(E)}$$

According to these reactions, the rate of formation of nitrous acid vapor can be expressed by the equation

$$R_{HNO_2} = 2k_E K_D (NO)(NO_2)(H_2O) - 2k_E'(HNO_2)^2 \quad . \quad (10)$$

This equation still predicts third-order kinetics for the initial reaction, but the requirement of a three-body collision is not made. The value of the equilibrium constant, K_D, calculated from the data of Hisatsune, is 11.9 atm^{-1} at 25°C. The concentration of N_2O_3 in the reaction mixtures was appreciable. For concentrations of 10 and 50 ppm of nitrogen dioxide and nitric oxide, respectively, the equilibrium concentration of N_2O_3 would be about 5×10^{-4} ppm (2×10^{-11} moles $liter^{-1}$) at 25°C. The second-order rate constant, k_E, is equal to

$$k_E = k_B/K_D \quad . \qquad (11)$$

The value of k_E was 6.9×10^4 liter $mole^{-1}$ sec^{-1} at 40°C. Values at 45° and 50°C are listed in Table 3. Although the third-order rate constant, k_B, did not change measurably with temperature, the second-order rate constant increased rapidly with temperature. The activation energy for reaction (E), calculated from the values of k_E at 40°, 45° and 50°C, was 10.2 ($\pm$ 3.5) kilocalories.

VI. DISCUSSION OF RESULTS

A. Introduction

The oxidation of nitric oxide in the presence of water vapor was studied at parts-per-million concentration of nitric oxide, percent concentrations of oxygen, and at ambient temperature and pressure. No specific catalytic effect of water was observed.

Three principal reactions were believed to occur:

$$2NO + O_2 = 2NO_2 \quad , \qquad (A)$$

$$NO + NO_2 + H_2O = 2HNO_2 \quad , \qquad (B)$$

$$3NO_2 + H_2O = NO + 2HNO_3 \quad . \qquad (C)$$

The reaction conditions were chosen such that reaction (C) occurred only to a very small extent. The dry oxidation was studied separately. Precise experimental data for three concentrations of nitric oxide and one concentration of oxygen were obtained for six temperatures from 25° to 50°C. The wet oxidation was studied at the same concentrations of nitric oxide and oxygen as in the dry oxidation, but water was added at three different concentrations. There were minor surface effects below 35°C. These were eliminated by raising the temperature to 40°C or higher.

B. Surface Effects

The rate of the wet oxidation increased measurably as the surface-to-volume ratio of the reactor increased.

The mechanism of catalysis is unknown. It is thought that nitric oxide and oxygen are dissolved in the multilayer film of water on the glass surface. The adsorbed-phase oxidation of nitric oxide then occurs at a faster rate than in the gas phase. The relatively sudden elimination of the surface activity by raising the reactor temperature is thought due to the reduction of multilayer adsorption. It is known that water remains adsorbed on glass well above 40°C. It was concluded that the interactions of the reactant gases do not depend merely on the adsorption of the gases directly on the surface. Hasche[12] also observed that the rate of the wet oxidation was greater than that of the dry oxidation in a glass reactor. He reported an increase in rate of 50 percent, which is far greater than found in the present work. Greig and Hall[9] found opposite behavior, reporting that, at 20°C, nitrogen dioxide remained adsorbed on the surface. They reported that the rate of oxidation of nitric oxide was unaffected.

C. The Formation of Nitrous Acid Vapor

The rate of formation of nitrous acid vapor was measured by comparing the concentration profile of nitrogen dioxide for both wet and dry oxidation runs. The value of the third-order rate constant, k_B, was found primarily by fitting the data at 40°C. Figure 9 shows the variation of some predicted profiles for nitrogen dioxide as the value of k_B was changed. If reaction (B) were very fast ($k_B \geq$

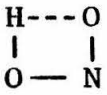
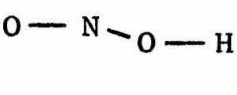
5×10^6 liter^2 mole^{-2} sec^{-1}), the reaction would not follow the behavior of the dry oxidation near the beginning of the reaction. If the reaction were very slow ($k_B \leq 1.5 \times 10^4$), the reaction would not deviate measurably from the third-order profile for the dry oxidation throughout the time interval studied. The behavior of the reaction shows that the rate of reaction represented by k_B is between the two extremes.

The rate of formation of nitrous acid vapor was also studied by Wayne and Yost[28]. Their results predicted a reaction rate about 300 times greater than that found in the present work. In their studies, the concentrations of nitric oxide and nitrogen dioxide were about three orders of magnitude greater than those encountered in the present study. The observed reaction rates were roughly six orders of magnitude apart. As such, it is not surprising that agreement between the two experiments is poor.

The overall role of water in the oxidation of nitric oxide is a small one. Concentrations of water up to 1.2 percent (9.1 mm Hg) changed the concentration of nitrogen dioxide by only about 14 percent after 50 minutes. Treacy and Daniels[21] found no detectable change in the oxidation when they added up to 0.5 mm Hg of water vapor to their low-pressure system. This is consistent with the present work since no appreciable reaction would occur at such a low concentration of water vapor.

D. Mechanism of Formation of Nitrous Acid Vapor

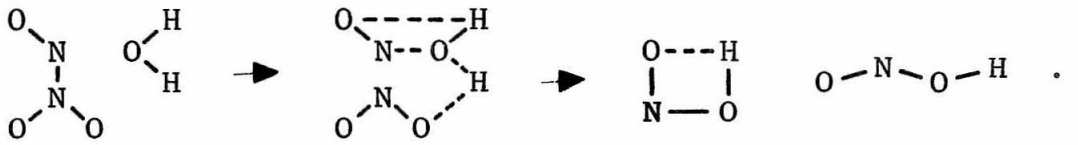
Nitrous acid vapor occurs in two isomeric forms, cis and trans:


(cis),

(trans) .

The isomers have been characterized by spectroscopy in the ultraviolet and infrared regions by several investigators including Hall and Pimentel[11] and Jones, Badger and Moore[14]. The stereochemical mechanism for the reaction which was assumed rate-controlling,

$$N_2O_3 + H_2O = 2HNO_2 \quad , \qquad (E)$$

probably proceeds according to the steps,



Thus, both cis and trans isomers are formed. The decomposition and formation of nitrous acid vapor must then proceed by the collision of two dissimilar molecules. The mechanism for the decomposition includes the reactions

$$HNO_2(cis) = HNO_2(trans) \qquad (F)$$

$$HNO_2(cis) + HNO_2(trans) = N_2O_3 + H_2O \qquad (G)$$

$$N_2O_3 = NO + NO_2 \quad . \qquad (H)$$

At higher temperatures, the trans isomer is favored in terms of thermodynamics. As the concentration of the cis isomer

decreases, the decomposition may become slower. The present measurements demonstrated that the overall rate of formation of nitrous acid vapor did not change appreciably from 40° to 50°C. This behavior was attributed in the previous section to the concentration of the reactive intermediate, N_2O_3, which increases with increasing temperature. An alternate explanation for the same behavior would be given by the mechanism,

$$NO + NO_2 = N_2O_3 \qquad \text{(fast)} \qquad \text{(D)}$$

$$N_2O_3 + H_2O = HNO_2(\text{cis}) + HNO_2(\text{trans}) \qquad \text{(fast)} \quad \text{(I)}$$

$$HNO_2(\text{cis}) + M = HNO_2(\text{trans}) + M \quad , \quad \text{(slow)} \qquad \text{(J)}$$

where M represents a molecule which provides the isomerization energy. There are no data available which describe the rate of isomerization. Since the present study was made at atmospheric pressure, however, the reactions were not considered as limited by energy transfer.

The kinetics of the oxidation of nitric oxide in the presence of water vapor were not greatly different from those of the dry oxidation. This fact is significant because it confirms that the overall reaction,

$$2NO + H_2O + 3/2\ O_2 = 2HNO_3 \quad , \qquad \text{(K)}$$

did not occur at an appreciable rate. This reaction, according to thermodynamics, goes to completion in the gas phase. One mechanism for reaction (K) might be,

$$2NO + O_2 = 2NO_2 \qquad (A)$$

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (B)$$

$$NO_2 + HNO_2 = NO + HNO_3 \quad . \qquad (L)$$

If reaction (L) occurred at a significant rate, the wet oxidation would have followed kinetics according to the equation,

$$R_{NO_2} = k_A(NO)^2(O_2) - k_B(NO)(NO_2)(H_2O) \quad .$$

No equilibrium would be established for nitrous acid, and the time-concentration profile for nitrogen dioxide would fall quickly from the dry behavior.

The importance of nitrous acid vapor lies mainly in its role as a stable intermediate in gas-phase reactions involving oxides of nitrogen and oxygenated compounds. The reaction of nitrogen dioxide with acetaldehyde,

$$CH_3CHO + NO_2 = CH_3CO\cdot + HNO_2 \quad ,$$

is one instance where nitrous acid is involved in a chain-initiating reaction. It also is a necessary intermediate in the formation and decomposition of nitric acid. Nitrous acid does not appear to be the strong reducing agent in the gas phase that it is in aqueous solution. This is indicated by the failure of the vapor to be oxidized directly by nitrogen dioxide or by oxygen.

VII. SUMMARY OF RESULTS

A. The oxidation of Nitric Oxide

The oxidation of nitric oxide was studied at atmospheric pressure and at ambient temperature. Parts-per-million concentrations of nitric oxide reacted with percent concentrations of oxygen. The reaction conditions were similar to those encountered in air. The third-order rate constant for the reaction, k_A, defined by the equation,

$$d(NO)/dt = -k_A(NO)^2(O_2) \quad , \qquad (2)$$

was equal to 1.46 ($\pm$ 0.03) x 10^4 liter^2 mole^{-2} sec^{-1} at 25°C. The activation energy for the reaction was -1.197 ($\pm$ 0.05) kilocalories. This value was determined in the range of temperature from 25° to 50°C. No deviations from third-order behavior were found. The reaction was observed, however, only to about 10 percent completion. There were no appreciable surface effects.

B. The Oxidation of Nitric Oxide in the Presence of Water

The oxidation of nitric oxide in the presence of water vapor was studied. The reaction conditions were identical to those in the studies of the dry oxidation. This facilitated the comparison of the two studies. Water vapor had no specific catalytic effect in the gas phase. When water was adsorbed in large quantities on the reactor surface, it increased the rate of oxidation slightly. The effects

could be eliminated by raising the reaction temperature to 40°C. At this temperature and above, the oxidation of nitric oxide, measured by the rate of formation of nitrogen dioxide, appeared to decrease in rate. It was assumed that the rate of oxidation of nitric oxide by oxygen was unchanged, and that nitrous acid vapor was formed by the overall reaction,

$$NO + NO_2 + H_2O = 2HNO_2 \quad . \qquad (B)$$

The rate of this reaction was calculated by comparing the relative rates of the wet and dry oxidations. The rate of formation of nitrous acid vapor is expressed in terms of the equation

$$R_{HNO_2} = 2k_B(NO)(NO_2)(H_2O) - 2k_B'(HNO_2)^2 \quad . \quad (10)$$

The value of k_B at 40°C was 1.5 ($\pm$ 0.5) x 10^5 liter^2 mole^{-2} sec^{-1}. The value of k_B' at 40°C was 1.1 x 10^4 liter^2 mole^{-2} sec^{-1}.

The present experiment, along with that described in Part I of this thesis, represents an integrated study of the gas-phase interactions of nitric oxide, oxygen, nitrogen dioxide and water vapor. The presence of a single phase was ensured by using very low concentrations of reactants. Surface effects were minor, and were eliminated by raising the reaction temperature slightly.

The rate of formation of nitrous acid vapor from parts-per-million concentrations of nitric oxide and nitrogen

dioxide was measured for the first time. The measured rate was about 300 times slower than that found by Wayne and Yost[28] who measured the rate at percent concentrations of the two oxides. Neither study presents conclusive evidence as to the mechanism of the reaction.

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Table 1. The Equilibrium Formation of Nitrous Acid Vapor

Date	Investigator	Temp (°C)	Equilibrium Pressures, mm Hg							K_P (atm^{-1})
			NO	NO_2	H_2O	N_2O_3	N_2O_4	HNO_2	HNO_3	
1950	Wayne and Yost	25								1.65
1961	Ashmore and Tyler	20	510.5	15.50	12.90	8.00	3.40	13.70	0.041	1.56
		40								0.64
		60								0.25
		80	440.8	17.70	98.80	0.44	0.05	10.65	0.039	0.11
		(25)								1.26
1962	Karavaev	25								1.60
1963	Waldorf and Babb	24	605.7	2.40	9.80	0.94	0.07	7.08		1.47
		(25)								1.38

Table 2. Predicted Concentrations for the Direct Formation of Nitrous Acid Vapor.

Data:

$$NO + NO_2 + H_2O \overset{k_B}{=} 2HNO_2 \qquad (B)$$

$k_B = 1.5 \times 10^5$ liter^2 mole^{-2} sec^{-1}

$K_B = 26.7$ liter mole^{-1}

$(NO)_o = 4.090 \times 10^{-6}$ moles liter^{-1}

Concentrations (moles liter^{-1})

	$(NO_2)_o = 4.090 \times 10^{-6}$			$(NO_2)_o = 4.090 \times 10^{-7}$		
Time (sec)	(NO) x10^6	(NO_2) x10^6	(HNO_2) x10^8	(NO) x10^6	(NO_2) x10^7	(HNO_2) x10^8
0	4.090	4.090	0.0	4.090	4.090	0.0
200	4.071	4.071	3.856	4.088	4.070	0.407
400	4.057	4.057	6.621	4.086	4.050	0.798
600	4.049	4.049	8.178	4.084	4.032	1.160
800	4.045	4.045	8.937	4.083	4.016	1.485
1000	4.044	4.044	9.282	4.081	4.002	1.770
1200	4.043	4.043	9.433	4.080	3.989	2.012
1400	4.042	4.042	9.498	4.079	3.979	2.213
1600	4.042	4.042	9.526	4.078	3.971	2.379
1800	4.042	4.042	9.539	4.077	3.964	2.512
2000	4.042	4.042	9.544	4.077	3.959	2.618

Table 3. Summary of Calculated and Experimental Results

$$2NO + O_2 = 2NO_2 \quad (A)$$

$$NO + NO_2 + H_2O = 2HNO_2 \quad (B)$$

$$NO + NO_2 = N_2O_3 \quad (D)$$

$$N_2O_3 + H_2O = 2HNO_2 \quad (E)$$

Temperature (°C)	k_A (*)	k_B (*)	K_B (**)	k_B' (***)	K_D (***)	k_E (***)
25	1.46×10^4	(1.5×10^5)	26.72	(5.6×10^3)	11.91	(1.26×10^4)
30	1.40×10^4	(1.5×10^5)	21.17	(7.1×10^3)	9.20	(1.63×10^4)
35	1.35×10^4	(1.5×10^5)	16.94	(8.8×10^3)	7.62	(1.97×10^4)
40	1.31×10^4	1.5×10^5	13.64	1.1×10^4	5.60	2.68×10^4
45	1.27×10^4	1.5×10^5	10.99	1.4×10^4	4.41	3.40×10^4
50	1.26×10^4	1.5×10^5	8.91	1.7×10^4	3.50	4.29×10^4

(*): units of $liter^2\ mole^{-2}\ sec^{-1}$

(**): units of $moles\ liter^{-1}$

(***): units of $liter\ mole^{-1}\ sec^{-1}$

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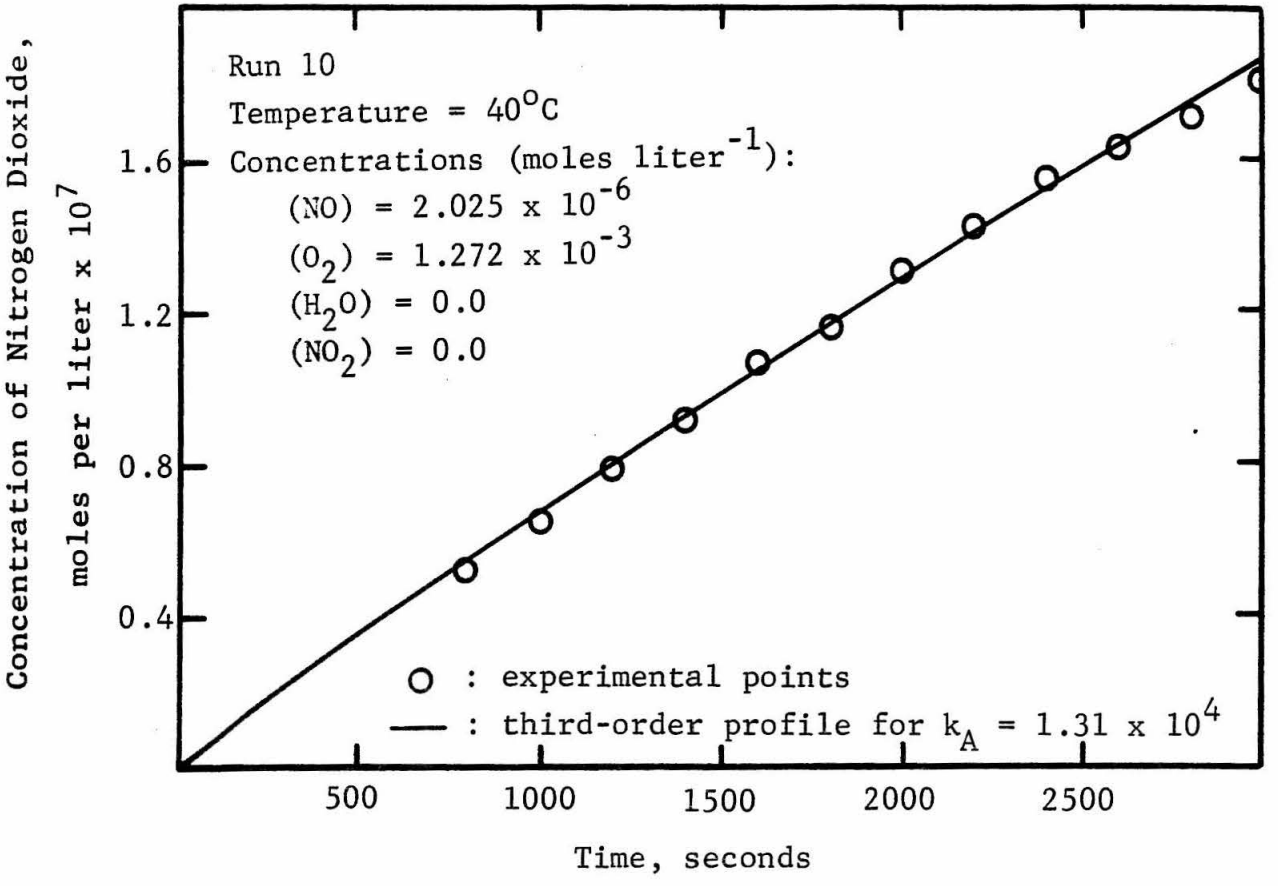

Figure 1. Time-Concentration Profile for Nitrogen Dioxide for the Oxidation of Nitric Oxide.

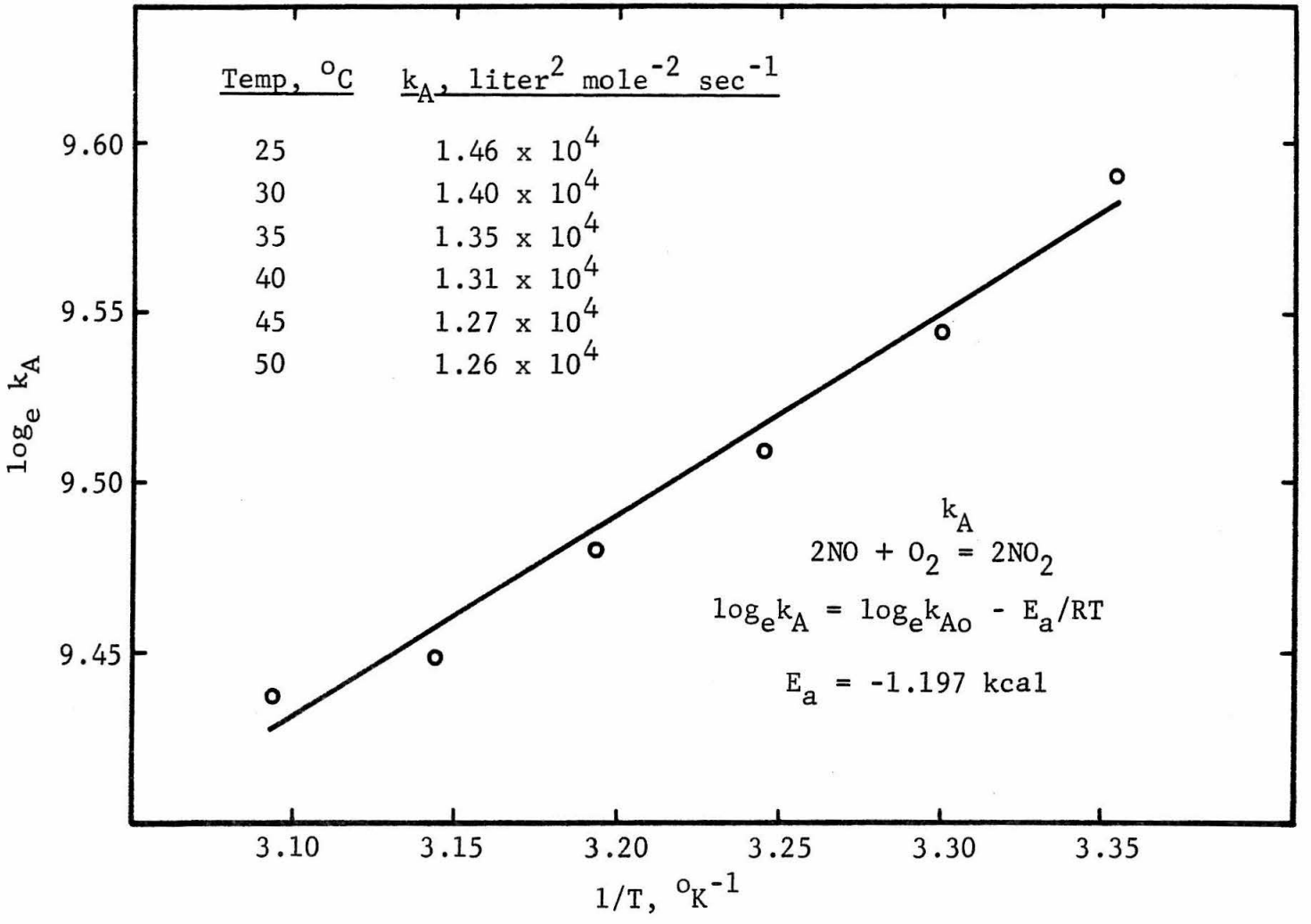

Figure 2. Arrhenius Plot for the Oxidation of Nitric Oxide

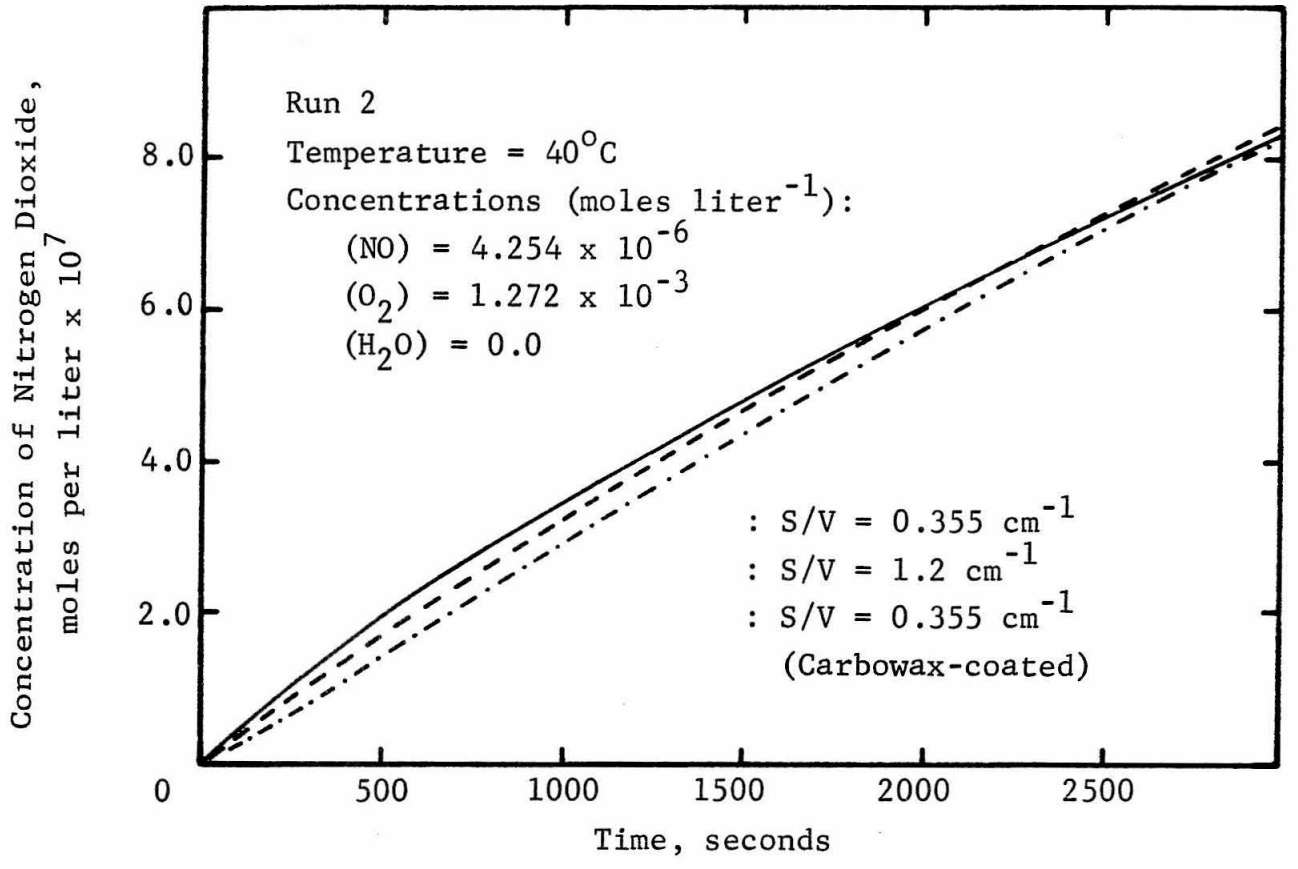

Figure 3. The Effect of Surface on the Thermal Oxidation of Nitric Oxide.

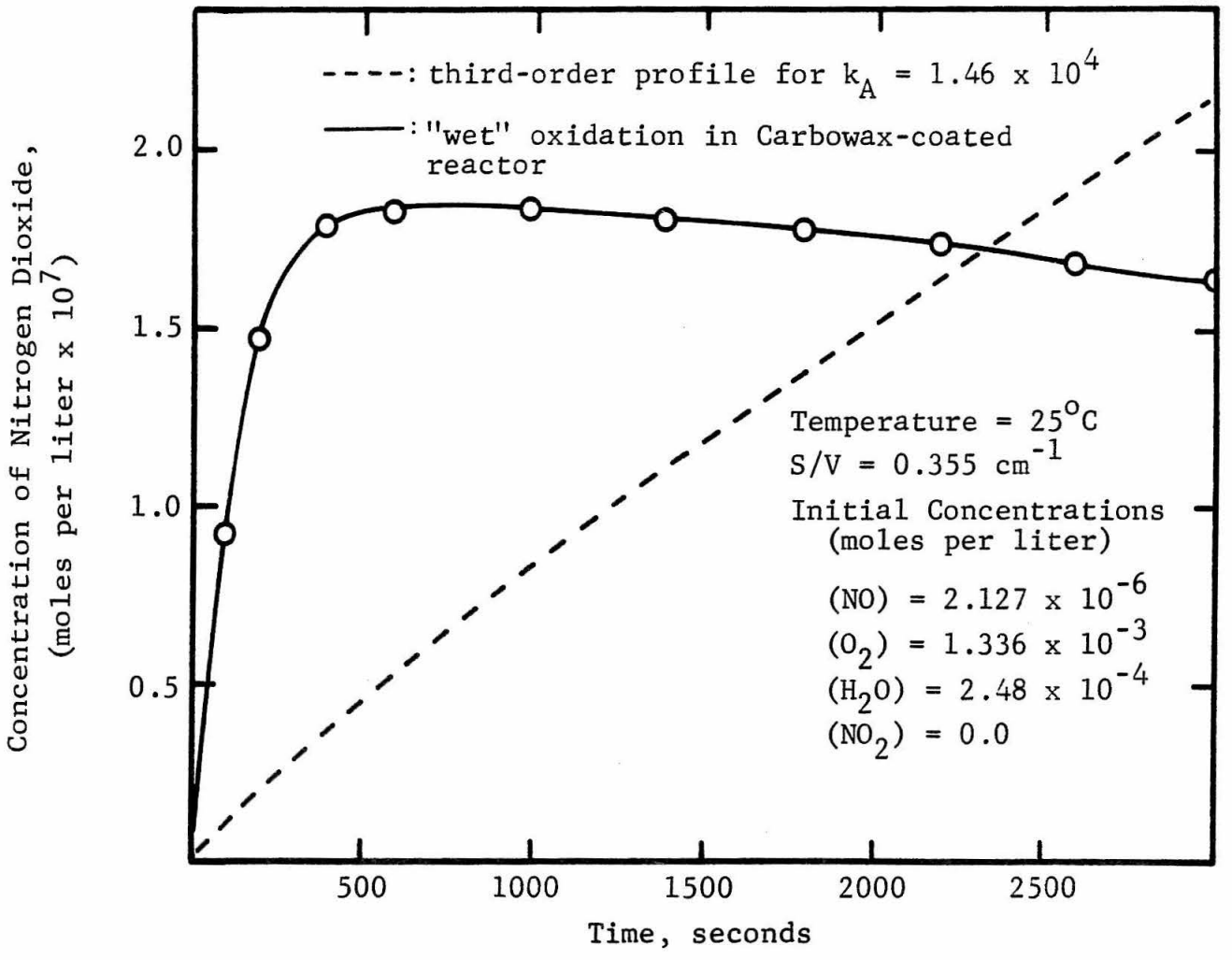

Figure 4. Catalysis of the Wet Oxidation of Nitric Oxide by a Surface Coated with Carbowax 5000.

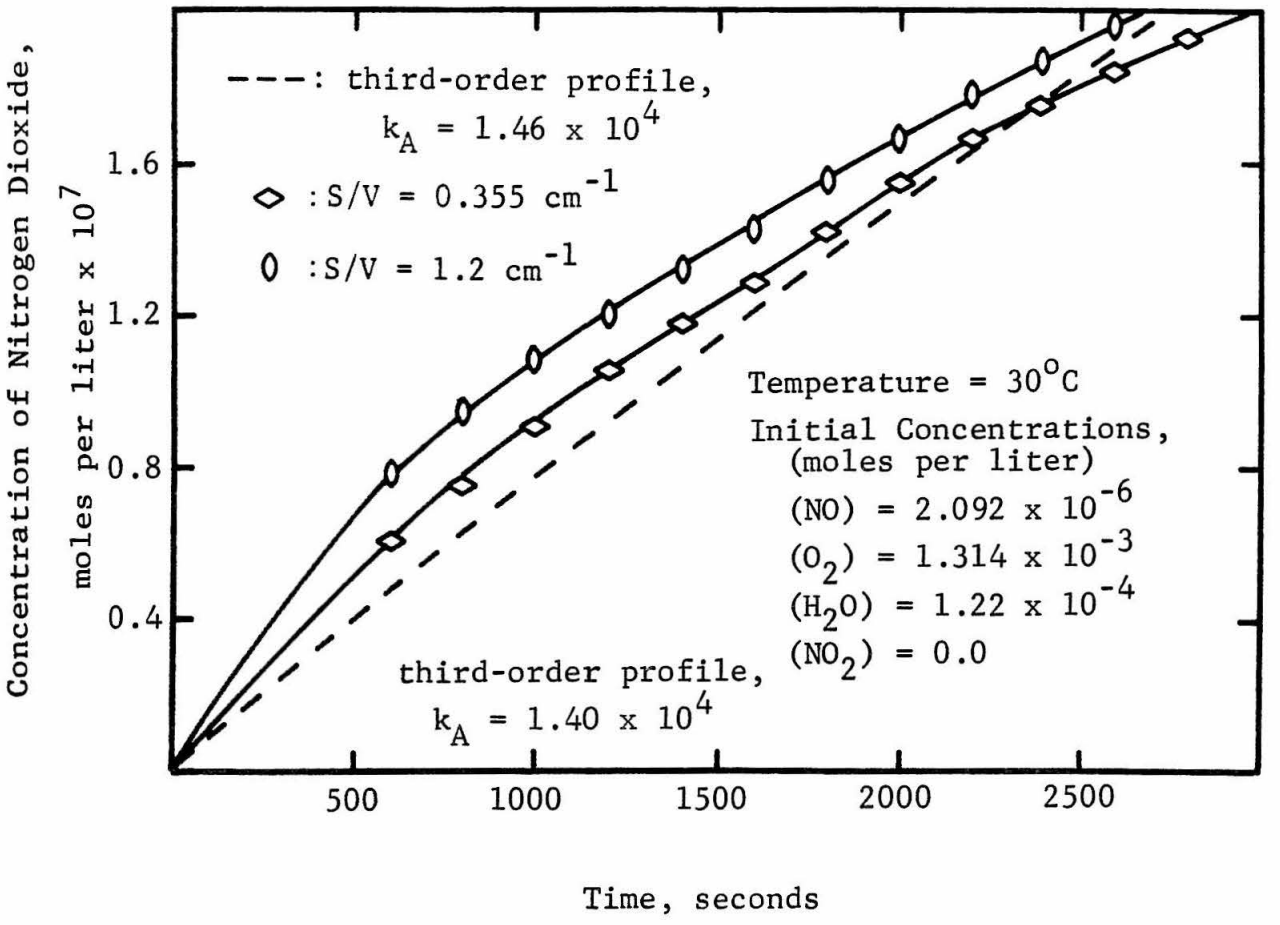

Figure 5. The Effect of Reactor Surface on the Wet Oxidation of Nitric Oxide.

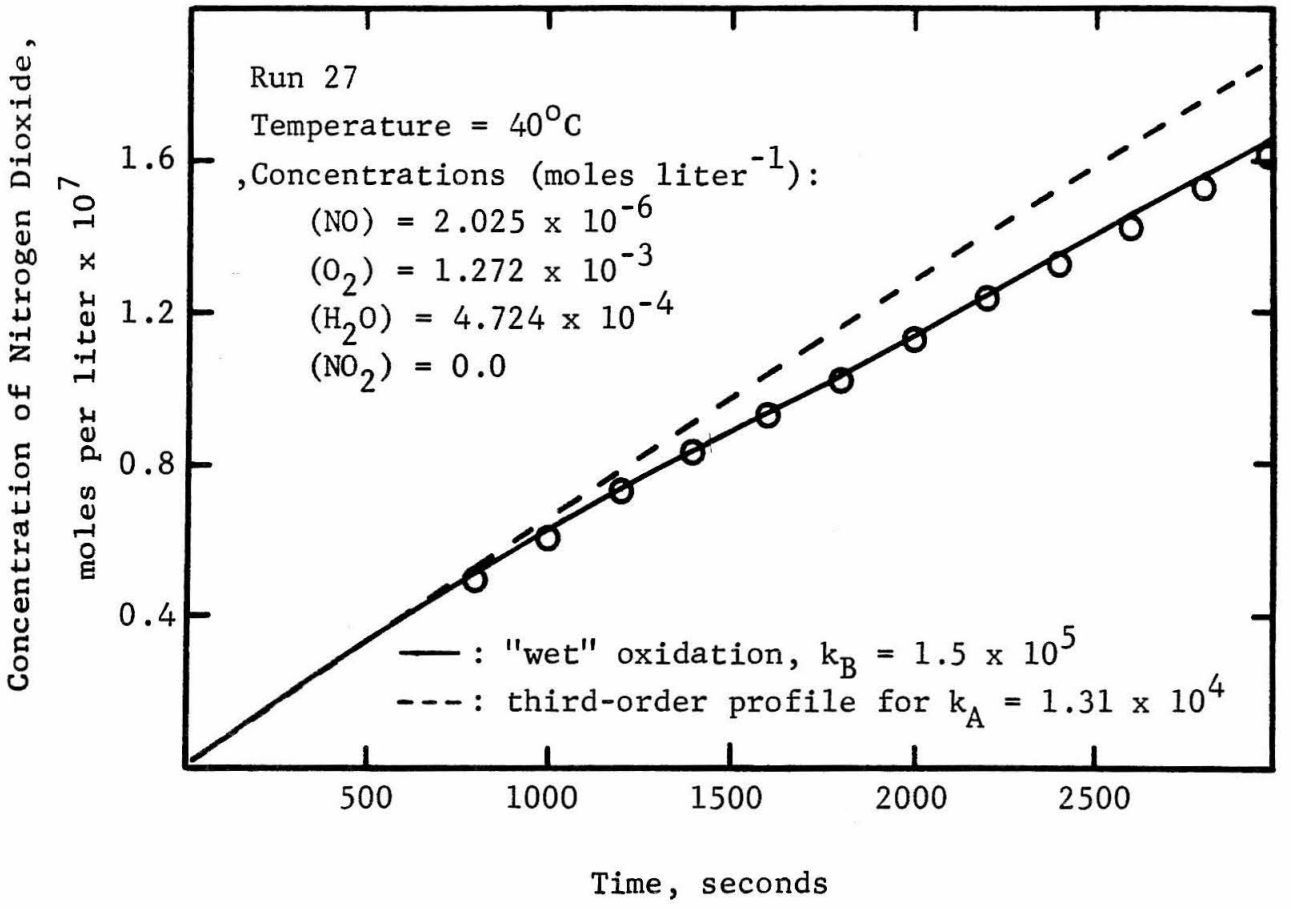

Figure 6. Experimental and Predicted Profiles for the Wet Oxidation of Nitric Oxide: 40°C.

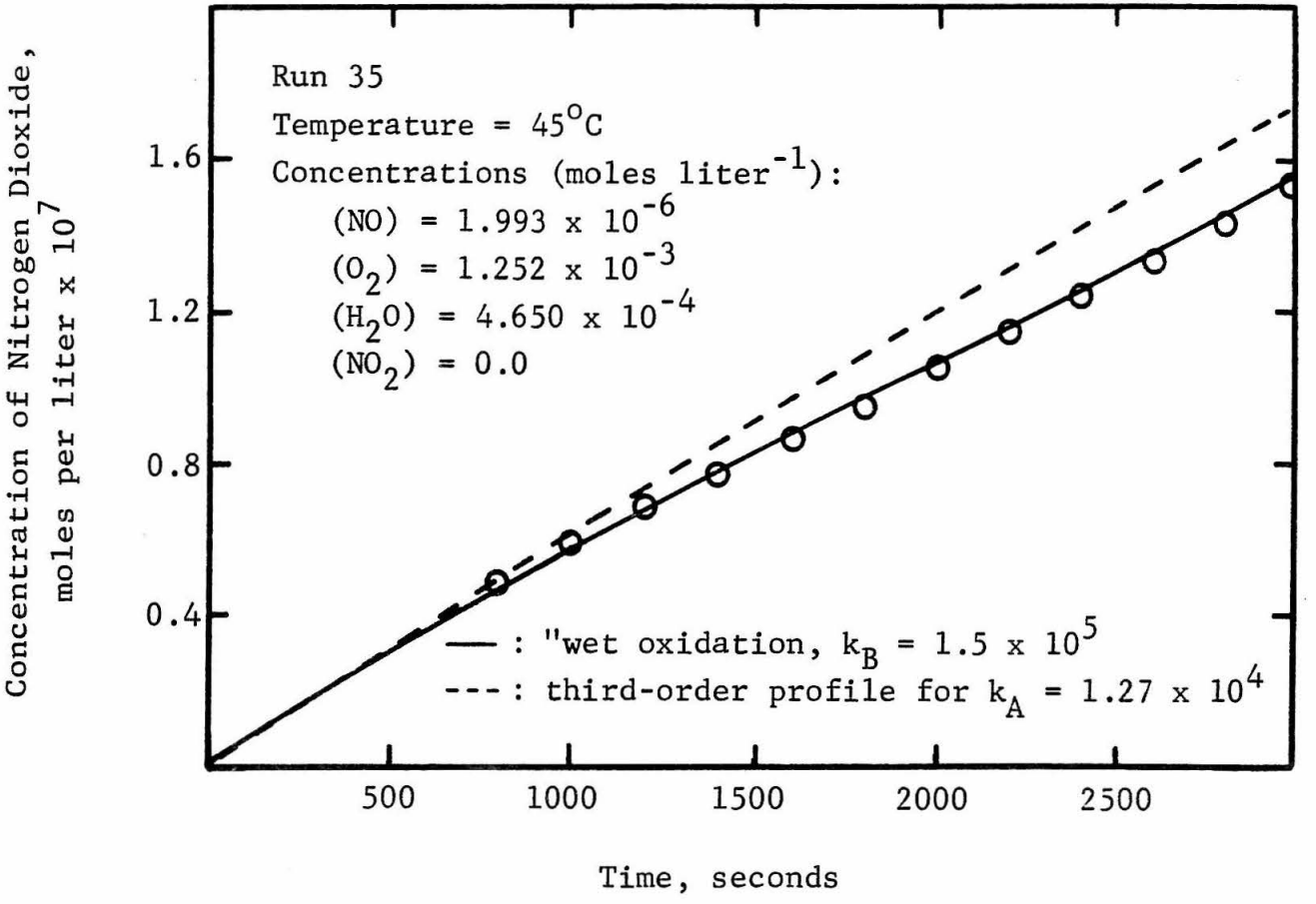

Figure 7. Experimental and Predicted Profiles for the Wet Oxidation of Nitric Oxide: 45°C.

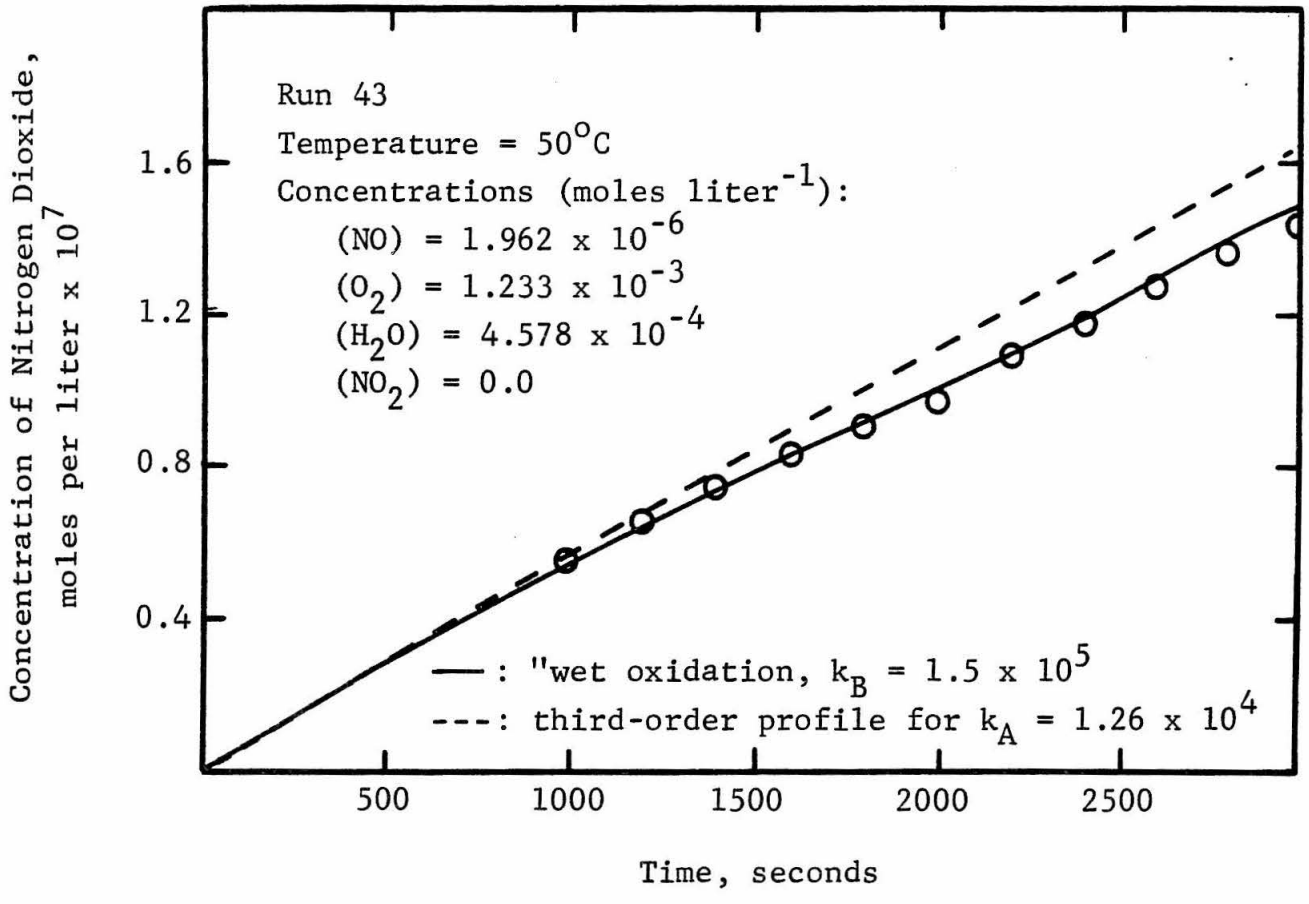

Figure 8. Experimental and Predicted Profiles for the Wet Oxidation of Nitric Oxide: 50°C.

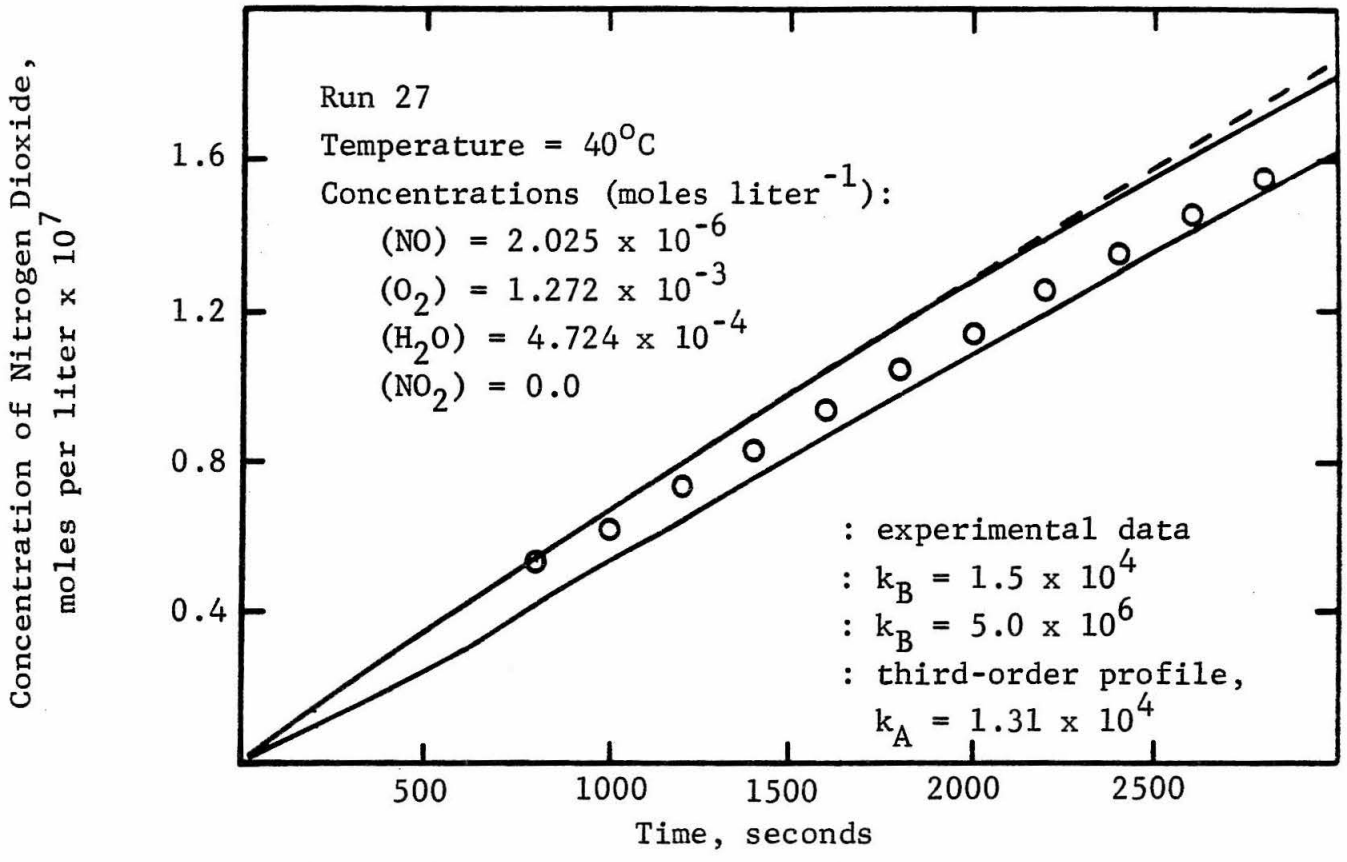

Figure 9. Change in Predicted Concentrations of Nitrogen Dioxide with the Rate of Formation of Nitrous Acid Vapor.

Appendix A. Experimental Data

Table 1. Summary of Initial Conditions for Experimental Runs

Run	Temp (°C)	Initial Concentrations (moles per liter) (NO) x10^6	(O_2) x10^3	(H_2O) x10^4
1	25	2.127	1.336	0.0
2	25	4.254	1.336	0.0
3	25	8.508	1.336	0.0
4	30	2.092	1.314	0.0
5	30	4.184	1.314	0.0
6	30	8.368	1.314	0.0
7	35	2.058	1.293	0.0
8	35	4.116	1.293	0.0
9	35	8.232	1.293	0.0
10	40	2.025	1.272	0.0
11	40	4.050	1.272	0.0
12	40	8.100	1.272	0.0
13	45	1.993	1.252	0.0
14	45	3.986	1.252	0.0
15	45	7.972	1.252	0.0
16	50	1.962	1.233	0.0
17	50	3.924	1.233	0.0
18	50	7.848	1.233	0.0
25	40	2.025	1.272	1.181
26	40	2.025	1.272	2.362
27	40	2.025	1.272	4.724

Table 1 (contd)

Run	Temp (^{o}C)	Initial Concentrations (moles per liter) (NO) x10^{6}	(O_2) x10^{3}	(H_2O) x10^{4}
28	40	4.050	1.272	1.181
29	40	4.050	1.272	2.362
30	40	4.050	1.272	4.724
33	45	1.993	1.252	1.162
34	45	1.993	1.252	2.325
35	45	1.993	1.252	4.650
36	45	3.986	1.252	1.162
37	45	3.986	1.252	2.325
38	45	3.986	1.252	4.650
41	50	1.962	1.233	1.144
42	50	1.962	1.233	2.289
43	50	1.962	1.233	4.578
44	50	3.924	1.233	1.144
45	50	3.924	1.233	2.289
46	50	3.924	1.233	4.578

Run 1

Initial Conditions

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.127 \times 10^{-6}$

$[O_2] = 1.336 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(min)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.19		0.175	
400	0.34		0.347	
600	0.50		0.517	
800	0.67		0.683	
1000	0.85		0.847	
1200	1.01		1.009	
1400	1.18		1.168	
1600	1.35		1.324	
1800	1.52		1.478	
2000	1.66		1.630	
2200	1.82		1.779	
2400	1.90		1.926	
2600	1.99		2.071	
2800	2.13		2.214	
3000	2.30		2.354	

Run 2

Initial Conditions

Reactor Temperature: 25°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.254 \times 10^{-6}$

$[O_2] = 1.336 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.69		0.694	
400	1.37		1.367	
600	2.10		2.018	
800	2.70		2.648	
1000	3.30		3.259	
1200	3.91		3.852	
1400	4.43		4.427	
1600	4.96		4.986	
1800	5.51		5.528	
2000	6.10		6.055	
2200	6.49		6.567	
2400	7.12		7.065	
2600	7.65		7.549	
2800	8.11		8.020	
3000	8.39		8.479	

Run 3

Initial Conditions

Reactor Temperature: 25.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 8.508 \times 10^{-6}$

$[O_2] = 1.336 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^8$
0	0.0		0.0	
200	0.29		0.273	
400	0.52		0.530	
600	0.79		0.770	
800	0.99		0.997	
1000	1.25		1.211	
1200	1.41		1.413	
1400	1.58		1.604	
1600	1.76		1.785	
1800	1.95		1.957	
2000	2.18		2.120	
2200	2.20		2.276	
2400	2.40		2.423	
2600	2.53		2.564	
2800	2.78		2.699	
3000	2.81		2.828	

Run 4

Initial Conditions

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.092 \times 10^{-6}$

$[O_2] = 1.314 \times 10^{-3}$

$[H_2O] = 0.0$

Concentrations (moles per liter)

Time	Experimental	Predicted		
	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.16		0.159	
400	0.31		0.316	
600	0.46		0.471	
800	0.62		0.623	
1000	0.77		0.773	
1200	0.92		0.920	
1400	1.09		1.067	
1600	1.28		1.210	
1800	1.39		1.352	
2000	1.41		1.491	
2200	1.68		1.629	
2400	1.71		1.764	
2600	1.93		1.898	
2800	2.08		2.030	
3000	2.11		2.160	

Run 5

Initial Conditions

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.184 \times 10^{-6}$

$[O_2] = 1.314 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.63		0.632	
400	1.24		1.246	
600	1.83		1.841	
800	2.41		2.420	
1000	2.91		2.982	
1200	3.58		3.528	
1400	4.07		4.060	
1600	4.51		4.576	
1800	5.01		5.078	
2000	5.51		5.568	
2200	6.10		6.044	
2400	6.43		6.508	
2600	6.89		6.960	
2800	7.35		7.401	
3000	7.89		7.831	

Run 6

Initial Conditions

Reactor Temperature: 30.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 8.368 \times 10^{-6}$

$[O_2] = 1.314 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^8$
0	0.0		0.0	
200	0.19		0.249	
400	0.42		0.484	
600	0.71		0.706	
800	0.93		0.915	
1000	1.13		1.114	
1200	1.37		1.302	
1400	1.40		1.480	
1600	1.55		1.650	
1800	1.89		1.812	
2000	2.04		1.966	
2200	2.22		2.112	
2400	2.31		2.253	
2600	2.42		2.387	
2800	2.52		2.515	
3000	2.62		2.638	

Run 7

Initial Conditions

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.058 \times 10^{-6}$

$[O_2] = 1.293 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.15		0.146	
400	0.30		0.291	
600	0.43		0.434	
800	0.58		0.574	
1000	0.70		0.713	
1200	0.85		0.849	
1400	0.99		0.984	
1600	1.11		1.117	
1800	1.23		1.248	
2000	1.33		1.378	
2200	1.43		1.505	
2400	1.60		1.631	
2600	1.73		1.756	
2800	1.88		1.878	
3000	2.03		2.000	

Run 8

Initial Conditions

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.116 \times 10^{-6}$

$[O_2] = 1.293 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.59		0.582	
400	1.15		1.148	
600	1.61		1.699	
800	2.15		2.234	
1000	2.70		2.755	
1200	3.24		3.262	
1400	3.80		3.757	
1600	4.24		4.238	
1800	4.63		4.707	
2000	5.13		5.165	
2200	5.68		5.611	
2400	6.08		6.046	
2600	6.49		6.470	
2800	6.81		6.885	
3000	7.22		7.290	

Run 9

Initial Conditions

Reactor Temperature: 35.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 8.232 \times 10^{-6}$

$[O_2] = 1.293 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^7$
0	0.0		0.0	
200	0.23		0.230	
400	0.45		0.447	
600	0.64		0.652	
800	0.83		0.848	
1000	1.01		1.033	
1200	1.11		1.209	
1400	1.35		1.377	
1600	1.54		1.537	
1800	1.69		1.690	
2000	1.86		1.386	
2200	2.05		1.975	
2400	2.15		2.109	
2600	2.32		2.237	
2800	2.41		2.359	
3000	2.51		2.477	

Run 10

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.025 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.13		0.136	
400	0.26		0.270	
600	0.39		0.402	
800	0.52		0.532	
1000	0.65		0.661	
1200	0.79		0.788	
1400	0.92		0.913	
1600	1.07		1.037	
1800	1.16		1.160	
2000	1.31		1.280	
2200	1.42		1.400	
2400	1.55		1.517	
2600	1.63		1.633	
2800	1.71		1.748	
3000	1.81		1.861	

Run 11

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.050 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.51		0.539	
400	1.04		1.064	
600	1.59		1.576	
800	2.12		2.074	
1000	2.59		2.560	
1200	3.06		3.034	
1400	3.55		3.496	
1600	3.99		3.947	
1800	4.31		4.387	
2000	4.78		4.816	
2200	5.16		5.236	
2400	5.55		5.645	
2600	6.00		6.046	
2800	6.39		6.437	
3000	6.75		6.819	

Run 12

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 8.100 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^8$
0	0.0		0.0	
200	0.20		0.213	
400	0.40		0.415	
600	0.61		0.607	
800	0.82		0.789	
1000	0.99		0.963	
1200	1.08		1.129	
1400	1.29		1.287	
1600	1.49		1.439	
1800	1.68		1.583	
2000	1.77		1.722	
2200	1.87		1.854	
2400	1.99		1.982	
2600	2.12		2.104	
2800	2.27		2.222	
3000	2.40		2.334	

Run 13

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.993 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.12		0.125	
400	0.25		0.249	
600	0.38		0.371	
800	0.51		0.492	
1000	0.61		0.611	
1200	0.71		0.729	
1400	0.83		0.845	
1600	0.94		0.960	
1800	1.03		1.074	
2000	1.21		1.186	
2200	1.34		1.297	
2400	1.42		1.407	
2600	1.55		1.515	
2800	1.64		1.622	
3000	1.75		1.728	

Run 14

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.986 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.50		0.498	
400	1.01		0.984	
600	1.55		1.458	
800	2.01		1.921	
1000	2.41		2.372	
1200	2.82		2.813	
1400	3.23		3.244	
1600	3.60		3.665	
1800	4.11		4.076	
2000	4.44		4.478	
2200	4.90		4.871	
2400	5.26		5.255	
2600	5.63		5.632	
2800	6.02		6.000	
3000	6.40		6.360	

Run 15

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 7.972 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^8$
0	0.0		0.0	
200	0.20		0.197	
400	0.40		0.384	
600	0.58		0.563	
800	0.74		0.733	
1000	0.91		0.896	
1200	1.07		1.051	
1400	1.23		1.200	
1600	1.37		1.342	
1800	1.53		1.479	
2000	1.64		1.610	
2200	1.77		1.736	
2400	1.88		1.857	
2600	2.09		1.974	
2800	2.13		2.086	
3000	2.23		2.194	

Run 16

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.962 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.12		0.118	
400	0.22		0.235	
600	0.32		0.351	
800	0.48		0.465	
1000	0.58		0.578	
1200	0.70		0.690	
1400	0.81		0.800	
1600	0.91		0.909	
1800	0.99		1.017	
2000	1.12		1.123	
2200	1.23		1.228	
2400	1.36		1.332	
2600	1.49		1.435	
2800	1.59		1.537	
3000	1.71		1.638	

Run 17

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.924 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0		0.0	
200	0.47		0.471	
400	0.94		0.930	
600	1.31		1.379	
800	1.75		1.818	
1000	2.22		2.246	
1200	2.66		2.665	
1400	3.07		3.074	
1600	3.44		3.475	
1800	3.91		3.866	
2000	4.21		4.249	
2200	4.67		4.624	
2400	5.06		4.991	
2600	5.35		5.350	
2800	5.70		5.702	
3000	5.99		6.047	

Run 18

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 7.848 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 0.0$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^8$
0	0.0		0.0	
200	0.20		0.186	
400	0.32		0.364	
600	0.52		0.533	
800	0.68		0.695	
1000	0.81		0.800	
1200	0.99		0.998	
1400	1.15		1.140	
1600	1.29		1.277	
1800	1.47		1.408	
2000	1.61		1.503	
2200	1.71		1.655	
2400	1.80		1.771	
2600	1.89		1.883	
2800	1.99		1.991	
3000	2.07		2.096	

Run 25

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.025 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 1.181 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	2.025	0.0	0.0
200	(0.13)	2.011	0.135	0.001
400	(0.27)	1.998	0.268	0.038
600	(0.40)	1.984	0.398	0.085
800	(0.52)	1.971	0.525	0.149
1000	(0.65)	1.958	0.649	0.229
1200	0.77	1.945	0.771	0.324
1400	0.89	1.932	0.891	0.432
1600	1.01	1.919	1.009	0.551
1800	1.12	1.906	1.124	0.679
2000	1.24	1.893	1.238	0.813
2200	1.35	1.880	1.349	0.952
2400	1.45	1.868	1.459	1.092
2600	1.56	1.856	1.568	1.233
2800	1.66	1.844	1.675	1.371
3000	1.76	1.832	1.781	1.505

Run 26

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.025 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 2.362 \times 10^{-4}$

Concentrations (moles per liter)

Time	Experimental	Predicted		
	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	2.025	0.0	0.0
200	(0.15)	2.011	0.135	0.019
400	(0.27)	1.998	0.266	0.076
600	(0.40)	1.984	0.393	0.169
800	(0.52)	1.970	0.517	0.294
1000	0.65	1.957	0.638	0.449
1200	0.75	1.943	0.756	0.628
1400	0.87	1.930	0.871	0.828
1600	0.98	1.916	0.983	1.042
1800	1.09	1.903	1.094	1.265
2000	1.20	1.890	1.202	1.490
2200	1.30	1.877	1.310	1.712
2400	1.40	1.864	1.415	1.927
2600	1.51	1.852	1.520	2.132
2800	1.61	1.839	1.624	2.325
3000	1.71	1.827	1.727	2.503

Run 27

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 2.025 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 4.724 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	2.025	0.0	0.0
200	(0.13)	2.011	0.134	0.038
400	(0.27)	1.997	0.262	0.151
600	(0.40)	1.983	0.385	0.331
800	(0.50)	1.969	0.503	0.571
1000	0.61	1.955	0.617	0.860
1200	0.72	1.940	0.727	1.185
1400	0.83	1.926	0.834	1.531
1600	0.93	1.912	0.939	1.885
1800	1.03	1.898	1.043	2.233
2000	1.13	1.885	1.146	2.566
2200	1.24	1.872	1.248	2.876
2400	1.33	1.858	1.349	3.161
2600	1.43	1.846	1.451	3.419
2800	1.53	1.833	1.552	3.651
3000	1.62	1.821	1.653	3.860

Run 28

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.050 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 1.181 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	4.050	0.0	0.0
200	(0.55)	3.998	0.535	0.077
400	1.05	3.942	1.049	0.298
600	1.55	3.889	1.543	0.648
800	2.04	3.837	2.018	1.102
1000	2.51	3.786	2.476	1.627
1200	2.88	3.736	2.919	2.185
1400	3.30	3.688	3.350	2.741
1600	3.75	3.640	3.771	3.267
1800	4.15	3.594	4.184	3.744
2000	4.55	3.550	4.588	4.164
2200	4.90	3.506	4.984	4.527
2400	5.31	3.464	5.374	4.840
2600	5.70	3.423	5.755	5.108
2800	6.08	3.384	6.130	5.338
3000	6.40	3.345	6.497	5.541

Run 29

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.050 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 2.362 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	4.050	0.0	0.0
200	(0.55)	3.995	0.532	0.152
400	1.05	3.941	1.035	0.588
600	1.50	3.886	1.512	1.257
800	1.98	3.832	1.966	2.085
1000	2.45	3.780	2.404	2.980
1200	2.85	3.728	2.830	3.854
1400	3.25	3.679	3.248	4.649
1600	3.60	3.631	3.658	5.335
1800	3.99	3.584	4.063	5.912
2000	4.40	3.540	4.462	6.392
2200	4.74	3.496	4.854	6.799
2400	5.15	3.454	5.300	7.144
2600	5.51	3.414	5.618	7.443
2800	5.90	3.374	5.990	7.708
3000	6.25	3.335	6.352	7.945

Run 30

Initial Conditions

Reactor Temperature: 40.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 4.050 \times 10^{-6}$

$[O_2] = 1.272 \times 10^{-3}$

$[H_2O] = 4.724 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	4.050	0.0	0.0
200	(0.55)	3.995	0.524	0.030
400	0.97	3.938	1.006	0.114
600	1.45	3.881	1.454	0.237
800	1.92	3.824	1.879	0.377
1000	2.40	3.769	2.291	0.513
1200	2.80	3.717	2.699	0.632
1400	3.23	3.667	3.104	0.730
1600	3.58	3.618	3.506	0.809
1800	3.95	3.572	3.905	0.874
2000	4.25	3.527	4.297	0.929
2200	4.60	3.484	4.684	0.976
2400	4.93	3.442	5.063	1.017
2600	5.30	3.401	5.434	1.054
2800	5.65	3.361	5.798	1.088
3000	6.00	3.323	6.155	1.118

Run 33

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.993 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 1.162 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.993	0.0	0.0
200	(0.12)	1.980	0.125	0.009
400	(0.25)	1.968	0.247	0.034
600	(0.37)	1.956	0.367	0.076
800	(0.49)	1.943	0.485	0.134
1000	0.60	1.931	0.601	0.205
1200	0.72	1.919	0.714	0.290
1400	0.82	1.907	0.825	0.387
1600	0.92	1.895	0.935	0.493
1800	1.03	1.883	1.042	0.606
2000	1.14	1.871	1.148	0.725
2200	1.24	1.859	1.253	0.848
2400	1.34	1.848	1.356	0.971
2600	1.45	1.836	1.457	1.093
2800	1.55	1.825	1.558	1.213
3000	1.64	1.814	1.657	1.329

Run 34

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.993 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 2.325 \times 10^{-4}$

Concentrations (moles per liter)

Time	Experimental	Predicted		
	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.993	0.0	0.0
200	(0.12)	1.980	0.124	0.017
400	(0.25)	1.968	0.246	0.068
600	(0.37)	1.955	0.364	0.151
800	(0.49)	1.943	0.479	0.263
1000	0.59	1.930	0.591	0.402
1200	0.70	1.918	0.700	0.562
1400	0.80	1.905	0.807	0.740
1600	0.90	1.893	0.912	0.930
1800	1.00	1.880	1.016	1.126
2000	1.09	1.868	1.117	1.322
2200	1.20	1.856	1.218	1.516
2400	1.30	1.844	1.317	1.701
2600	1.40	1.833	1.416	1.877
2800	1.50	1.821	1.514	2.040
3000	1.59	1.810	1.611	2.191

Run 35

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.993 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 4.650 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.993	0.0	0.0
200	(0.12)	1.980	0.124	0.034
400	(0.25)	1.967	0.242	0.135
600	(0.37)	1.954	0.356	0.296
800	(0.48)	1.941	0.466	0.511
1000	0.58	1.928	0.572	0.769
1200	0.68	1.915	0.675	1.057
1400	0.77	1.902	0.775	1.363
1600	0.86	1.889	0.874	1.673
1800	0.95	1.876	0.971	1.975
2000	1.05	1.900	1.068	2.261
2200	1.14	1.851	1.164	2.526
2400	1.24	1.839	1.260	2.776
2600	1.33	1.828	1.356	2.984
2800	1.43	1.816	1.452	3.178
3000	1.53	1.805	1.547	3.353

Run 36

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.986 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 1.162 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.986	0.0	0.0
200	(0.51)	3.936	0.495	0.068
400	1.00	3.886	0.970	0.267
600	1.44	3.837	1.428	0.580
800	1.90	3.789	1.870	0.985
1000	2.30	3.742	2.297	1.451
1200	2.73	3.696	2.711	1.942
1400	3.12	3.650	3.115	2.426
1600	3.50	3.606	3.510	2.878
1800	3.92	3.563	3.898	3.284
2000	4.25	3.522	4.279	3.638
2200	4.60	3.481	4.653	3.942
2400	5.01	3.442	5.020	4.404
2600	5.35	3.404	5.381	4.426
2800	5.69	3.366	5.735	4.620
3000	6.05	3.330	6.083	4.790

Run 37

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.986 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 2.325 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.986	0.0	0.0
200	(0.51)	3.936	0.491	0.136
400	1.00	3.885	0.957	0.526
600	1.43	3.835	1.400	1.124
800	1.85	3.785	1.824	1.859
1000	2.24	3.736	2.234	2.644
1200	2.63	3.688	2.634	3.402
1400	3.00	3.642	3.026	4.080
1600	3.40	3.598	3.414	4.658
1800	3.80	3.555	3.796	5.141
2000	4.15	3.513	4.172	5.543
2200	4.50	3.473	4.543	5.881
2400	4.85	3.434	4.907	6.172
2600	5.20	3.395	5.264	6.426
2800	5.55	3.358	5.615	6.652
3000	5.83	3.322	5.959	6.856

Run 38

Initial Conditions

Reactor Temperature: 45.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.986 \times 10^{-6}$

$[O_2] = 1.252 \times 10^{-3}$

$[H_2O] = 4.650 \times 10^{-4}$

Concentrations (moles per liter)

	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.986	0.0	0.0
200	(0.51)	3.935	0.484	0.270
400	1.00	3.883	0.932	1.022
600	1.43	3.830	1.350	2.115
800	1.78	3.778	1.747	3.346
1000	2.16	3.727	2.136	4.322
1200	2.53	3.679	2.520	5.534
1400	2.88	3.632	2.903	6.356
1600	3.24	3.587	3.284	7.020
1800	3.65	3.544	3.660	7.563
2000	4.00	3.503	4.032	8.023
2200	4.35	3.462	4.397	8.422
2400	4.70	3.423	4.755	8.776
2600	5.01	3.384	5.107	9.096
2800	5.39	3.347	5.452	9.388
3000	5.70	3.310	5.790	9.656

Run 41

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.962 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 1.144 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.962	0.0	0.0
200	(0.12)	1.950	0.118	0.008
400	(0.23)	1.938	0.234	0.031
600	(0.34)	1.927	0.347	0.070
800	(0.46)	1.915	0.459	0.122
1000	0.56	1.903	0.568	0.188
1200	0.67	1.892	0.676	0.266
1400	0.78	1.880	0.782	0.353
1600	0.88	1.869	0.886	0.450
1800	0.99	1.858	0.988	0.553
2000	1.09	1.846	1.089	0.660
2200	1.18	1.836	1.188	0.770
2400	1.28	1.825	1.286	0.879
2600	1.37	1.814	1.383	0.987
2800	1.47	1.803	1.479	1.092
3000	1.55	1.793	1.574	1.192

Run 42

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.962 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 2.289 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.962	0.0	0.0
200	(0.12)	1.950	0.118	0.016
400	(0.23)	1.938	0.232	0.062
600	(0.34)	1.926	0.344	0.138
800	(0.46)	1.914	0.453	0.241
1000	0.56	1.902	0.559	0.367
1200	0.67	1.890	0.663	0.513
1400	0.77	1.878	0.765	0.675
1600	0.86	1.867	0.865	0.845
1800	0.95	1.855	0.964	1.020
2000	1.05	1.844	1.061	1.195
2200	1.20	1.832	1.157	1.364
2400	1.30	1.821	1.252	1.525
2600	1.40	1.810	1.346	1.676
2800	1.50	1.800	1.440	1.816
3000	1.59	1.789	1.534	1.944

Run 43

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 1.962 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 4.578 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	1.962	0.0	0.0
200	(0.12)	1.950	0.117	0.032
400	(0.23)	1.938	0.229	0.124
600	(0.34)	1.926	0.337	0.271
800	(0.45)	1.913	0.441	0.468
1000	0.55	1.901	0.542	0.702
1200	0.67	1.888	0.640	0.963
1400	0.74	1.876	0.736	1.237
1600	0.83	1.864	0.831	1.512
1800	0.92	1.852	0.924	1.777
2000	0.98	1.840	1.017	2.025
2200	1.10	1.828	1.110	2.252
2400	1.19	1.817	1.203	2.457
2600	1.28	1.806	1.295	2.640
2800	1.37	1.795	1.387	2.804
3000	1.45	1.785	1.479	2.950

Run 44

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.924 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 1.144 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.924	0.0	0.0
200	(0.45)	3.877	0.468	0.063
400	0.91	3.830	0.918	0.245
600	1.36	3.784	1.352	0.531
800	1.80	3.738	1.771	0.900
1000	2.22	3.693	2.178	1.320
1200	2.60	3.649	2.573	1.758
1400	2.95	3.606	2.959	2.184
1600	3.35	3.564	3.327	2.575
1800	3.69	3.524	3.708	2.932
2000	4.05	3.484	4.074	3.220
2200	4.40	3.446	4.432	3.475
2400	4.75	3.409	4.785	3.693
2600	5.10	3.372	5.131	3.880
2800	5.40	3.336	5.471	4.043
3000	5.75	3.302	5.805	4.186

Run 45

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.924 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 2.289 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.924	0.0	0.0
200	(0.45)	3.876	0.464	0.125
400	0.90	3.829	0.906	0.482
600	1.35	3.781	1.327	1.027
800	1.80	3.734	1.731	1.691
1000	2.20	3.688	2.122	2.390
1200	2.55	3.643	2.505	3.052
1400	2.90	3.600	2.881	3.633
1600	3.27	3.558	3.253	4.123
1800	3.65	3.517	3.620	4.528
2000	3.97	3.477	3.982	4.864
2200	4.32	3.439	4.338	5.149
2400	4.65	3.401	4.687	5.495
2600	4.95	3.365	5.031	5.611
2800	5.30	3.329	5.368	5.806
3000	5.63	3.294	5.698	5.982

Run 46

Initial Conditions

Reactor Temperature: 50.0°C

Concentrations of Reactants (moles per liter):

$[NO] = 3.924 \times 10^{-6}$

$[O_2] = 1.233 \times 10^{-3}$

$[H_2O] = 4.578 \times 10^{-4}$

	Concentrations (moles per liter)			
	Experimental	Predicted		
Time	$[NO_2]$	$[NO]$	$[NO_2]$	$[HNO_2]$
(sec)	$\times 10^7$	$\times 10^6$	$\times 10^7$	$\times 10^8$
0	0.0	3.924	0.0	0.0
200	(0.45)	3.876	0.458	0.247
400	0.90	3.826	0.883	0.935
600	1.35	3.777	1.281	1.926
800	1.78	3.728	1.662	3.024
1000	2.18	3.680	2.035	4.050
1200	2.55	3.634	2.405	4.914
1400	2.88	3.590	2.775	5.608
1600	3.23	3.548	3.141	6.165
1800	3.56	3.508	3.504	6.624
2000	3.80	3.468	3.860	7.014
2200	4.15	3.429	4.211	7.356
2400	4.49	3.392	4.556	7.662
2600	4.85	3.355	4.894	7.940
2800	5.02	3.320	5.226	8.194
3000	5.40	3.285	5.552	8.428

PROPOSITIONS

PROPOSITION I

It is proposed to employ the streaming potential in a detection system for use with liquid chromatography. The concentration of solvent impurities in the effluent of a liquid-solid adsorption column is detected by measuring the streaming potential of the flowing fluid. Equations are presented that relate the concentration of these impurities in the effluent to the streaming potential. Under several restrictive assumptions, the streaming potential of acetone flowing through a quartz plug may be described by the equation

$$E = 5.02 \times 10^{-2} \exp(-7.75 \times 10^{2} \sqrt{C})\, \Delta P$$

where E is the streaming potential in volts, ΔP is the pressure drop across the plug in mm Hg, and C is the concentration of impurities in moles per liter.

Introduction

Elution chromatography carried out in the liquid phase is a common analytical tool of chemists and biochemists. A multicomponent sample is separated into bands by an adsorption column, and the effluent of the column is analyzed for the presence and strength of these bands.

For colorless substances, identification of the bands requires the ability to note changes in the properties of the effluent. Commonly measured properties include refractive index, pH, conductivity, fluorescence, infrared absorption, radioactivity, chemical properties, and the dielectric constant. These properties are often measured from small samples taken from a "fraction collector," a mechanical device that collects the effluent in small fractions. Each fraction is analyzed separately so that the band may be extended over several fractions.

In addition to the previous methods of identification, it is proposed the streaming potential of the flowing column effluent be measured. The streaming potential varies with the concentration of the sample component in the band. For dilute systems, this property may give an accurate and sensitive determination of components in a liquid sample.

Application of streaming potential to liquid chromatography requires that a solvent exhibiting streaming potential be used in the adsorption column. Acetone exhibits

a streaming potential large enough to be measured easily.

Development

When a poorly conducting liquid is forced through a capillary, a potential is developed across the capillary which is proportional to the pressure difference (Quincke's law)[1]. The voltage is called the streaming potential. The classical equation describing the streaming potential is the Helmholtz-Smoluchowski equation:

$$\frac{E}{\Delta P} = \frac{D \zeta}{4\pi \mu k} \quad , \tag{1}$$

where E is the streaming potential, ΔP is the pressure difference across the capillary, D is the dielectric constant of the fluid, μ is the viscosity of the fluid, k is the electrical conductivity of the fluid, and ζ is the zeta potential. The zeta potential arises out of the theory of the electrical double layer which is thought to cause the streaming potential. Ions in a solution may interact with a capillary wall and form layers of charges over the surface of the wall. The wall may be charged or it may simply adsorb one type of ion preferentially. When a liquid flows through the capillary, the ions in the outer layer may be carried along with the fluid flow causing a net flow of charge downstream. This flow is known as the streaming current. The streaming potential is the voltage measured across the capillary when there is no streaming current.

For small values of the electrical forces at the wall, the potential through the double layer is given by

$$\psi = \psi_o \exp(-\chi Y) \qquad (2)$$

where ψ is the measured potential, ψ_o is the potential at the wall, Y is the distance from the wall, and χ is a function of concentration equal to

$$\chi = \sqrt{\frac{8\pi Z^2 F^2 C}{DRT}} \qquad (3)$$

where Z is the valence of the ion, F is Faraday's constant, C is the concentration of the ion, and D is the dielectric constant. Equations (2) and (3) are the Gouy-Chapman equations for the diffuse double layer at a plane interface[2]. The zeta potential is defined in terms of equation (2); when $Y = 1/\chi$, $\zeta = \psi = 0.368\,\psi_o$. Then

$$\psi = \frac{\zeta}{0.368} \exp(-\chi Y) = 2.7\zeta \exp(-\chi Y) \qquad (4)$$

It is desired to relate these equations to a situation that may be encountered in liquid-solid chromatography. Specifically, an organic solvent such as acetone will be forced through a capillary and its streaming potential will be measured. From time to time, a band of some substance will be eluted from the adsorption column, and when it passes through the capillary the streaming potential across the capillary will change.

The steady-state streaming potential for the solvent is

given by equation (1). It is assumed that when a band of impurity enters the capillary, the substance becomes the principal charge-carrying species. This is justified since non-aqueous solvents, except for the lower alcohols, may have only very small separations of charge. Under this assumption the steady-state variables are redesignated with superscript zeroes; ζ^o is the steady-state zeta potential for the solvent, χ^o is the reciprocal of the steady-state double layer thickness, Y^o is the double layer thickness and equals $1/\chi^o$. A new zeta potential is defined equal to

$$\zeta = \zeta^o \exp(-\chi Y^o) \tag{5}$$

where ζ is the new zeta potential and is a function of the steady-state and of the concentration of the new charge-carrying species. From equation (3) it is seen that if the concentration of impurity is zero, the zeta potential reduces to that of steady state.

The streaming potential may be calculated from

$$\frac{E}{\Delta P} = \frac{D\zeta^o \exp(-\chi Y^o)}{4\pi\mu k} \tag{6}$$

where

$$\chi = \sqrt{\frac{8\pi Z^2 F^2 C}{DRT}} \tag{7}$$

or simply

$$\frac{E}{\Delta P} = K \exp(-\chi Y^o) \quad . \tag{8}$$

Thus the streaming potential may be expected to vary exponentially as the square root of the impurity concentration in the solvent. This result assumes isothermal conditions with the product being the principal charge-carrying species present.

The Gouy-Chapman equations are developed by considering that ionic species are present, and that the distribution of these ions is described by the Boltzmann law,

$$C_i = C_{io} \exp\ (-\ Z_i F \psi / RT) \quad . \qquad (9)$$

There may be considerable inaccuracy describing non-aqueous solvents that exhibit streaming potential by this equation. The linear relationship of streaming potential with pressure has been confirmed, and specifically, Lorenz[3] has presented good experimental results for the acetone-quartz system.

Experimental

An apparatus similar to that of Lorenz[3] may be used to measure the streaming potential. Acetone is forced across a quartz plug and the potential is measured across the plug. The electrodes are platinum. Lorenz used a pressure-decline technique for his measurements which implies that the system equilibrated quickly to the changing pressure. Although in the proposed method the pressure drop is constant, it may be expected that the response of the streaming potential to changing concentrations will also be rapid and near equilibrium.

Calculation

In order to predict what the sensitivity of the proposed method would be, it is necessary to determine

$$\frac{E}{\Delta P} = \frac{D\xi^{o}\exp(-\chi Y^{o})}{4\pi\mu k} \tag{6}$$

with regard to the solvent, acetone. Specifically, Y^{o} must be determined, and since $Y^{o} = 1/\chi^{o}$, χ^{o} must be found. The value of χ^{o} is given by the equation

$$\chi^{o} = \sqrt{\frac{8\pi Z^{2}F^{2}C^{o}}{DRT}} \tag{10}$$

or equivalently

$$\chi^{o} = \sqrt{\frac{8\pi Z^{2}e^{2}n}{DkT}} \tag{11}$$

where n is the number of ions per cubic centimeter, e is the electronic charge, and k is Boltzmann's constant. For non-aqueous solvents it is normally supposed that ionization takes place only to a very limited extent. Thus n, the ion concentration, must be replaced by a significant term for the solvent. It is supposed that non-aqueous solvents that exhibit streaming potential have some ionic character. As an order of magnitude approximation, the specific conductivity of acetone is taken as representative of the contribution of this ionic character. Assuming that the ionic concentration is approximately proportional to the specific conductivity, the ionic concentration is estimated by

$$n_{acetone} = \frac{k_{acetone}}{k_{water}} \times n_{water}$$

$$= \frac{2.0 \times 10^{-7}}{1.7 \times 10^{-6}} \times 10^{-7}$$

$$= 1.2 \times 10^{-8} \text{ moles/liter} \quad .$$

Taking Z equal to unity,

$$\chi^{o} = \sqrt{\frac{8\pi e^2 n}{DkT}} \quad .$$

In electrostatic cgs units and at 25°C,

$$\chi_o = \sqrt{\frac{8\pi (4.774 \times 10^{-10})^2 (1.2 \times 10^{-8})(6.02 \times 10^{23})}{(1000)(1.38 \times 10^{-16})(298)}}$$

$$= \sqrt{1.0 \times 10^{10}}$$

$$= 1.0 \times 10^{5} \text{ cm}^{-1} \quad .$$

From equation (6), the term $D\zeta^{o}/4\pi\mu k$ is just the streaming potential per unit pressure drop for pure acetone for which Lorenz determined a value of 38.1 microvolts per barye. The value of χ is given by

$$\chi = \sqrt{\frac{8\pi (4.774 \times 10^{-10})^2 (6.02 \times 10^{23})\ C}{(1000)(1.38 \times 10^{-16})(298)}}$$

$$= \sqrt{1.2 \times 10^{-8}\ C}$$

$$= 1.1 \times 10^{-4} \sqrt{C}$$

where C is expressed in ions per liter. Then

$$\frac{E}{\Delta P} = 38.1 \exp\left(-1.1 \times 10^{-9} \sqrt{C}\right) \text{ microvolts/barye.}$$

For C expressed in moles per liter, ΔP in mm Hg, and E in volts, this corresponds to

$$\frac{E}{\Delta P} = 5.0 \times 10^{-2} \exp\left(-7.8 \times 10^{2} \sqrt{C}\right) \text{ volts/mm Hg.}$$

For small concentrations,

$$\frac{E}{\Delta P} = 5.0 \times 10^{-2} \left(1-7.8 \times 10^{2} \sqrt{C}\right) \text{ volts/mm Hg.}$$

The change in streaming potential with concentration describes the sensitivity of the proposed method. The sensitivity is

$$\frac{d(E/\Delta P)}{dC} = -19.5/\sqrt{C} \text{ volt liter/mole mm Hg .}$$

Electro-osmotic Pressure

For a non-flow system, the electro-osmotic pressure could be measured in place of the streaming potential. The electro-osmotic pressure is related to the streaming potential by the phenomenological equations which describe electrokinetic properties:

$$I = C_{11}E + C_{12}P \qquad (12)$$

$$V = C_{21}E + C_{22}P \quad ,$$

where I is the electrical current, E is the potential across a capillary or plug, P is the pressure drop across the plug, and V is the volumetric flow rate through the plug. The streaming potential is

$$S = (E/P)_{I=0} = -C_{12}/C_{11} \quad .$$

The electro-osmotic pressure is

$$P_E = (P/E)_{V=0} = -C_{21}/C_{22} \quad .$$

If the coefficients C_{12} and C_{21} bear the proper relationship to the production of entropy, then

$$C_{12} = C_{21} \quad .$$

The electro-osmotic pressure may be expressed as

$$P_E = S\ (C_{11}/C_{22})(C_{21}/C_{12}) \quad ,$$

where C_{11} is the electrical conductivity, and C_{22} is the constant which relates the pressure drop through a capillary or plug to the volumetric flow rate.

Lorenz[3] measured the conductance and permeability (C_{22}) of acetone flowing through a porous quartz plug. The value of C_{22} was

$$C_{22} = 6.31 \times 10^{-7}\ \text{cm}^3/\text{sec/barye} \quad ,$$

and for C_{11},

$$C_{11} = 4.0 \times 10^{-7}\ \text{ohm}^{-1} \quad .$$

Then the electro-osmotic pressure is

$$P_E = \frac{4.0 \times 10^{-7}}{6.3 \times 10^{-7}} \times [5.0 \times 10^{-2} \exp(-7.8 \times 10^2 \sqrt{C})]$$

$$= 1.84 \times 10^{-8} \exp(-7.8 \times 10^2 \sqrt{C})$$

For small concentrations of impurity in the solvent,

$$P_E = 1.84 \times 10^{-8} \left(1 - 7.8 \times 10^2 \sqrt{C} \right) \text{ mm Hg/volt} \quad .$$

The value for the electro-osmotic pressure is quite small, and it can be considered too small measure for systems encountered in liquid chromatography.

Discussion

Lorenz[3] states that the streaming potential exhibited by acetone is probably due to the presence of foreign ions from the solid (quartz) dissolved in the liquid. If this is the case, two responses of the streaming potential to a concentration change may appear.

If the entering substance interferes with the electrical double layer in such a way as to degrade it, the streaming potential will decrease. This is the case discussed previously. It may be imagined that the streaming potential will increase with changing concentration. If the streaming potential is due to the presence of foreign ions, then the response of the streaming potential to changing concentrations may be strengthened by the addition to acetone of a controlled amount of an ionic salt.

The experimental difficulties of stabilizing a flowing system where electrical measurements depend directly on the rate of flow are great. Such a limitation would be the principal difficulty with the proposed method of measurement.

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PROPOSITION II

A non-aqueous electrolyte was prepared from antimony tribromide and potassium bromide. When the solution was polarized, a chemical battery resulted which had a no-load potential of 0.8 volt. Development of the electrolyte resulted from a study of the bromides of tin, arsenic and antimony, all of which are salts melting under 100°C. The electrical conductivities of each compound were studied up to 150°C.

Introduction

A simple and convenient type of battery would be one in which the electrolyte was the salt of the anodic and cathodic materials. For example, if sodium chloride melted at low temperature, a battery could be made from the cell

$$Na \;/\; NaCl \;/\; Cl_2 \quad .$$

One practical application of this principle is the lithium-chlorine cell used by General Motors. Because of their strong ionic character, most salts do not melt except at high temperatures. This is usually at a temperature higher than the melting point of the corresponding metal. A few salts melt at relatively low temperatures, below $100^{o}C$. Among these are the halides of antimony, arsenic and tin.

The chlorine and bromine salts of these metals have a density between that of the liquid halogen and the metal. As a result, one conceivably could construct a gravity-layered battery with, for example, antimony on the bottom, antimony tribromide in the middle, and liquid bromine (with a carbon electrode) on the top.

The halogen salts of tin, arsenic and antimony would be poor electrolytes, however, because they are poor conductors of electricity. This is not surprising since one expects the melting point of a salt to increase with increasing ionic character. Thus, lithium chloride has a melting point of $613^{o}C$ while stannic bromide ($SnBr_4$) has a melting

point of 31°C.

There are at least two ways to increase the conductivity of a low-melting salt. The first is to raise its temperature. Since the conductivity of an insulator is nearly proportional to its temperature, this method limits the increase obtainable by this method to relatively small amounts, say by a factor of ten. The second way to increase the conductivity is to dissolve an ionic salt in the non-ionic material. This approach was taken in the present study.

The object of this study was to obtain a highly--conducting electrolyte consisting primarily of a low-melting salt of antimony, arsenic or tin. No similar studies have been reported in the literature. The experiment began by building some simple equipment with which to prepare and examine the electrolytes.

Experimental

A standard conductivity cell and bridge apparatus was used to measure the conductivities of the fused salts. The conductivity cell consisted of two 1/16-inch stainless-steel rods separated by two Teflon spacers. At the end of each rod were stainless-steel electrodes, separated by 0.3 cm, and each with a cross-sectional area of about 0.25 cm^2. A simple Wheatsone bridge using a pulsed voltage was used to measure the resistance of the electrolyte in the cell. A Tektronix Type 503 oscilloscope was used to detect the

null. The pulse was supplied by a simple unijunction transistor oscillator combined with a 27-volt DC power supply.

The temperature of the electrolyte during a measurement was controlled by an electrically-heated aluminum manifold. The manifold was a four-inch aluminum cylinder that had been bored to accommodate test tubes. Zircon cement enclosed the cylinder. Chromel resistance wire was wrapped around the cement and connected electrically to a variable transformer.

The bromine salts were prepared by the direct action of bromine on the metal. In the case of tin, the bromine was kept in excess to exclude the formation of stannous bromide, $SnBr_2$. Antimony trichloride was purchased from Baker. No further purification of the salts was made. A 0.100 N solution of potassium chloride was used to determine the cell constant for the conductivity cell.

Results

1. Antimony tribromide

Of the four fused salts examined, antimony tribromide was the highest melting (98.6°C) and the best conductor. The accompanying table lists the conductivity of the salt as a function of temperature. At 100°C, the conductivity was 1.5×10^{-5} ohm^{-1} cm^{-1}. Ordinary battery acid has a conductivity at room temperature of 0.77 ohm^{-1} cm^{-1}. The conductivity of the salt doubled when the temperature was raised to 150°C.

Potassium bromide was added to the fused antimony tribromide in amounts varying from three to six percent by weight. The change in conductivity is recorded in Table 1. as a function of temperature for the three-percent mixture. The conductivity of this mixture at 150°C was approximately 200-times higher than that of the pure salt. The ionic salt dissolved very slowly in the fused salt. It appeared at first that only very little of the potassium bromide would go into solution. After several days, however, the three-percent mixture was fully dissolved. The maximum solubility of potassium bromide in antimony tribromide has yet to be determined.

The chemistry of dissolution is unknown. It appears that the antimony tribromide forms a complex with the ionic salt. Ordinarily one would not expect appreciable amounts of a strong ionic salt to be dissolved since the solvent must supply sufficient energy to destroy the ionic crystal. This could be done by antimony tribromide only by complexing the potassium bromide, probably by removing bromide ions from the crystal. Plyushchev, et al[1] suggest that the compound $KBr:SbBr_3$ is formed, at least at high pressures.

A six-percent mixture of potassium bromide in antimony tribromide was prepared. The conductivity of this mixture is also included in the table. Experiments were performed on this mixture to determine the feasibility of building the battery:

$$Sb \;/\; SbBr_3\text{--}KBr \;/\; Br_2 \;/\; C \quad .$$

The conductivity cell was disconnected from the pulse generator, and polarized with the 27-volt DC supply. The polarizing voltage was removed and the output of the cell was measured. A typical characteristic is shown in Figure 1. The cell was capable of maintaining an open-circuit voltage of 0.8 volt, and a voltage under a 100-ohm load of 0.4 volt. for several minutes. This result was considered excellent in view of the poor applicability of the conductivity electrodes as a battery.

2. Arsenic Tribromide

Arsenic tribromide and arsenic tribromide with potassium bromide did not conduct appreciably. The conductivity bridge was limited to measuring resistances less than one megohm. The resistance of arsenic tribromide, even in the presence of potassium bromide, was greater than this value up to 150°C. It should be noted, however, that sufficient time may not have been allowed for the potassium bromide to dissolve. The rate of dissolution was not discovered to be slow until after the measurements on arsenic tribromide were made.

3. Stannic Bromide

The results with stannic bromide were identical with those of arsenic tribromide. The resistance of the fused salt, and that of the salt in the presence of potassium

bromide, was greater than one megohm. Again, the rate of dissolution of potassium bromide into the fused salt may have been a factor.

4. Antimony Trichloride

Some early experiments were made with antimony trichloride. This compound appeared to be unsuitable because of its high vapor pressure, and the tendency to disproportionate into antimony pentachloride ($SbCl_5$) and antimony. The conductivity of the pure salt was higher than that of the bromine salt. Quantitative measurements were not obtained because of experimental difficulties. Chiefly, these were associated with gold-wire electrodes used in an early conductivity cell. The antimony apparently formed an amalgam with the gold after being electrolyzed. The use of a low-voltage AC Wheatstone bridge did not prevent the amalgam from forming.

Discussion

The electrical properties of mixtures of antimony tribromide and potassium bromide have not been studied previously. The work done here suggests that the electrical properties of antimony tribromide and other non-conducting and low-melting salts may be enhanced by the addition of relatively small amounts of ionic salts. The application of these electrolytes to lower-temperature fused-salt batteries is apparent.

The electrolytes made in the present study are about

an order of magnitude poorer conductors than battery acid, and cannot be used as high-current electrolytes. Additional work is needed to study the effects of other ionic salts such as ammonium bromide or perhaps some bromate compounds with reference to increasing the conductivity. The limiting solubility of potassium bromide in antimony tribromide should also be determined.

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TABLE OF RESULTS

Solvent	Solute	Concentration	Temperature (^{o}C)	Conductivity ($ohm^{-1}cm^{-1}$)
Water	KCl	0.100 N	22°C	1.04×10^{-2}
$SbBr_3$			100	1.55×10^{-5}
			150	3.00×10^{-5}
$SbBr_3$	KBr	0.03 g/g	106	4.30×10^{-3}
			116	5.50×10^{-3}
			128	7.05×10^{-3}
			133	7.57×10^{-3}
			137	7.70×10^{-3}
			142	7.81×10^{-3}
			153	8.50×10^{-3}
$SbBr_3$	KBr	0.06 g/g	135	1.72×10^{-1}

PROPOSITION III

This proposition suggests that solid ionic conductors can be used as solid-state devices analogous to semiconductor devices. Advantage is taken of the property of silver [I] tetraiodomercurate [II] to change its crystalline state with temperature. It is suggested that this change in state, accompanied by a change in electrical conductivity, can be induced by the application of an electric field across such a crystal. The electrical properties of the crystal in its transition region would allow small changes in voltage to greatly change the conductivity of the crystal. As a result, the crystal could be used as an electrical amplifier. Equations are presented that relate the temperature of transition to the electric field needed to induce the transition.

Introduction

Silver [I] tetraiodomercurate [II], Ag_2HgI_4, changes from an electrical insulator to an electrical conductor at $50^{\circ}C$[1]. The transition is caused by a change in crystal structure which allows transfer of metal ions within the solid. In the low-temperature form, the mercury atoms occupy the corners of a face-centered cubic lattice while silver atoms are confined to four of the face-center positions[2]. The two vacant face-center positions are on parallel faces. In the high-temperature form, the corners and all six of the face centers are randomly occupied by both mercury and silver atoms. The number of metal ions is smaller than the number of lattice points among which they are distributed. Thus it is easy for the metal ions to move throughout the lattice simply by moving into unoccupied lattice sites. The electrical conductivity of the higher-temperature form is about ten times higher than that of the low-temperature form. The transition takes place sharply at a particular temperature.

Copper [I] tetraiodomercurate [II] is also a solid ionic conductor. Its transition temperature is about $67^{\circ}C$[1]. Mixtures of the copper and silver salts exhibit transition temperatures as low as $33^{\circ}C$. Other solid ionic conductors are CuI, CuBr and AgI (above $140^{\circ}C$).

The conductivity of Ag_2HgI_4 changes as a function of temperature as shown in Figure 1. The sharp rise in conductivity with temperature indicates the physical transition that occurs in the crystal. This property is analogous to the relationship between the volume and the temperature of a substance undergoing a phase transition, particularly a liquid-vapor transition. The position of this transition is dependent on pressure. From this analogy, it was thought that the position of the transition region for crystals of Ag_2HgI_4 could also be changed by changing external variables. In particular, if the transition temperature could be lowered to ambient temperature, advantage could be made of the large changes of conductivity which occur during the transition. It was thought that the application of a voltage across a crystal would supply some of the energy of transition. If the crystal were maintained in the transition region by this method, then small changes in the voltage would give large changes in the conductivity of the crystal. Thus, the crystal would act as an amplifier. The following section discusses the relationship of the applied voltage to the position of the transition with respect to temperature.

Theory

The electrical conductivity of Ag_2HgI_4 varies with temperature as shown in Figure 1. The discontinuity of the conductivity is an indication of a phase transition.

In general, the position of this transition point will change as a function of the system variables:

$$dF_{\alpha} = V_{\alpha}dP - S_{\alpha}dT + (dF/dE)_{\alpha}\, dE \qquad (1)$$

and

$$dF_{\beta} = V_{\beta}dP - S_{\beta}dT + (dF/dE)_{\beta}\, dE \qquad (2)$$

where α denotes the high-temperature phase, β denotes the low-temperature phase, and E represents the external electric field. At constant pressure and at equilibrium between the two phases:

$$dF_{\alpha} = dF_{\beta} \quad . \qquad (3)$$

Thus,

$$dE/dT = \Delta S/\Delta(dF/dE) \quad , \qquad (4)$$

where Δ is equal to $(\alpha-\beta)$. The quantity, (dF/dE), is proportional to the number of charge carriers, the constant relating the two being Faraday's constant. The number of charge carriers is in turn proportional to the conductivity. Thus,

$$\Phi = k_1\,(dF/dE) \quad . \qquad (5)$$

In addition, since the conductivity of the high-temperature form is much greater than that of the low-temperature form,

$$\Delta\Phi \simeq \Phi_{\alpha} \quad . \qquad (6)$$

Substituting into equation (4),

$$dE/dT = \Delta S/(k_1\Phi_{\alpha}) \quad . \qquad (7)$$

In addition, the conductivity may be described by the equation

$$\phi = \phi_o \exp(-\underline{E}/RT) \quad , \tag{8}$$

where $\underline{E}$ represents the activation energy needed to mobilize a metal atom in the crystal lattice. The entropy of transition is equal to the heat of transition divided by the transition temperature:

$$\Delta S = \Delta H/T \quad . \tag{9}$$

Therefore,

$$dE/dT = \left(\frac{\Delta H}{k_1 \phi_o}\right)\left[\frac{\exp(-\underline{E}/RT)}{T}\right] dT \tag{10}$$

Finally, the transition temperature and the electric field can be related by the equation

$$E = \int_{T_o}^{T} \left(\frac{\Delta H}{k_1 \phi_o}\right)\left[\frac{\exp(-\underline{E}/RT)}{T}\right] dT \quad , \tag{11}$$

where T_o is the transition temperature with no applied field (50°C for Ag_2HgI_4). The solution to equation (11) is

$$E = \left(\frac{\Delta H}{k_1 \phi_o}\right)\left[\ln \frac{T}{T_o} + \sum_{n=1}^{\infty} \left[\left(\frac{E}{RT_o} - \frac{E}{RT}\right)^n / n \cdot n!\right]\right] \tag{12}$$

Introducing the dimensionless quantities

$$\lambda = Ek_1\phi/\Delta H \tag{13}$$

and

$$\psi = RT/\underline{E} \tag{14}$$

equation (12) is reduced to

$$\lambda = \ln \frac{\psi}{\psi_o} + \sum_{n=1}^{\infty} [(\frac{1}{\psi_o} - \frac{1}{\psi})^n / n \cdot n!] \quad . \quad (15)$$

Equation (15) was solved for the case of Ag_2HgI_4 for which the value of ψ_o can be calculated. The results are presented in Table 1. The practical application depends on the value of k_1, the constant that relates the number of charge carriers to the conductivity. This quantity is unknown and must be determined experimentally. For useful application, the actual voltage should be on the order of one to 100 volts per cm at room temperature. Included in Table 1 are predicted values of voltage and temperature for various values of k_1. It can be seen that the value of k_1 in units of cal ohm cm volt^{-1} should be between one and 100.

Discussion

The applications for ionic conductors which undergo phase transitions would be analogous to transistors and other semiconductor devices, but would not require a pure crystal or the diffusion of impurities into crystals. In general, they would be devices which do not follow Ohm's law at the transition point. Their conductivity would be a strong function of the voltage applied to the crystal.

The possible applications of ionic-conducting crystals are not limited to those which depend on biasing the crystal. For example, the crystals could be used as switching devices

which activate at their transition temperature. An interesting possibility is the use of Ag_2HgI_4 crystals as bistable switches. For such an application a moderate biasing voltage would be applied across the crystal. The crystal would act as an insulator, and only a little current would flow. If a high-voltage pulse were then applied to the crystal, it would switch to the higher-conducting phase. The heat dissipation in the crystal would raise the local temperature above the transition temperature, and the crystal would continue to conduct. This conducting state could be changed by a negative-going pulse or by removal of the initial biasing voltage.

These applications depend on the physical and chemical characteristics of the ionic conducting crystals. The chemical and thermal stability of the crystals would be critical. The method of fabrication would also influence the electrical properties. Suchow and Pond[1] found that the conductivity was sensitive to the amount of compression used to prepare samples of Ag_2HgI_4.

REFERENCES

1. Suchow, L., and G. R. Pond, J. Am. Chem. Soc., 75, 5242(1953).

2. Ketelaar, J. A. A., Z. physik. Chem., B26, 327(1934).

see also:

Ketelaar, J. A. A., Trans. Faraday Soc., 34, 874(1938).

Table 1. Predicted Values for the Transition Temperature of Silver [I] Tetraiodomercurate [II]

Experimental Data (from Suchow and Pond[1]):

$\underline{E} = 7.4 \times 10^3$ cal

$\Delta H = 1.43 \times 10^3$ cal

$\Phi_o = 9.1$ ohm^{-1}cm^{-1}

ψ	λ	Temp (°C)	Predicted Voltages (volts) $k_1 = 1$	$k_1 = 100$
0.0779	2.092	17	328.7	3.287
0.0784	1.904	19	299.2	2.992
0.0789	1.728	21	271.5	2.715
0.0795	1.562	23	245.5	2.455
0.0800	1.406	25	221.0	2.210
0.0806	1.260	27	198.0	1.980
0.0811	1.122	29	176.2	1.762
0.0816	0.991	31	155.7	1.557
0.0822	0.867	33	136.2	1.362
0.0827	0.750	35	117.9	1.179
0.0832	0.639	37	100.4	1.004
0.0838	0.534	39	83.9	0.839
0.0843	0.434	41	68.2	0.682
0.0848	0.339	43	53.2	0.532
0.0853	0.248	45	39.0	0.390
0.0859	0.161	47	25.0	0.250
0.0865	0.079	49	12.4	0.124
0.0870	0.0	50	0.0	0.0

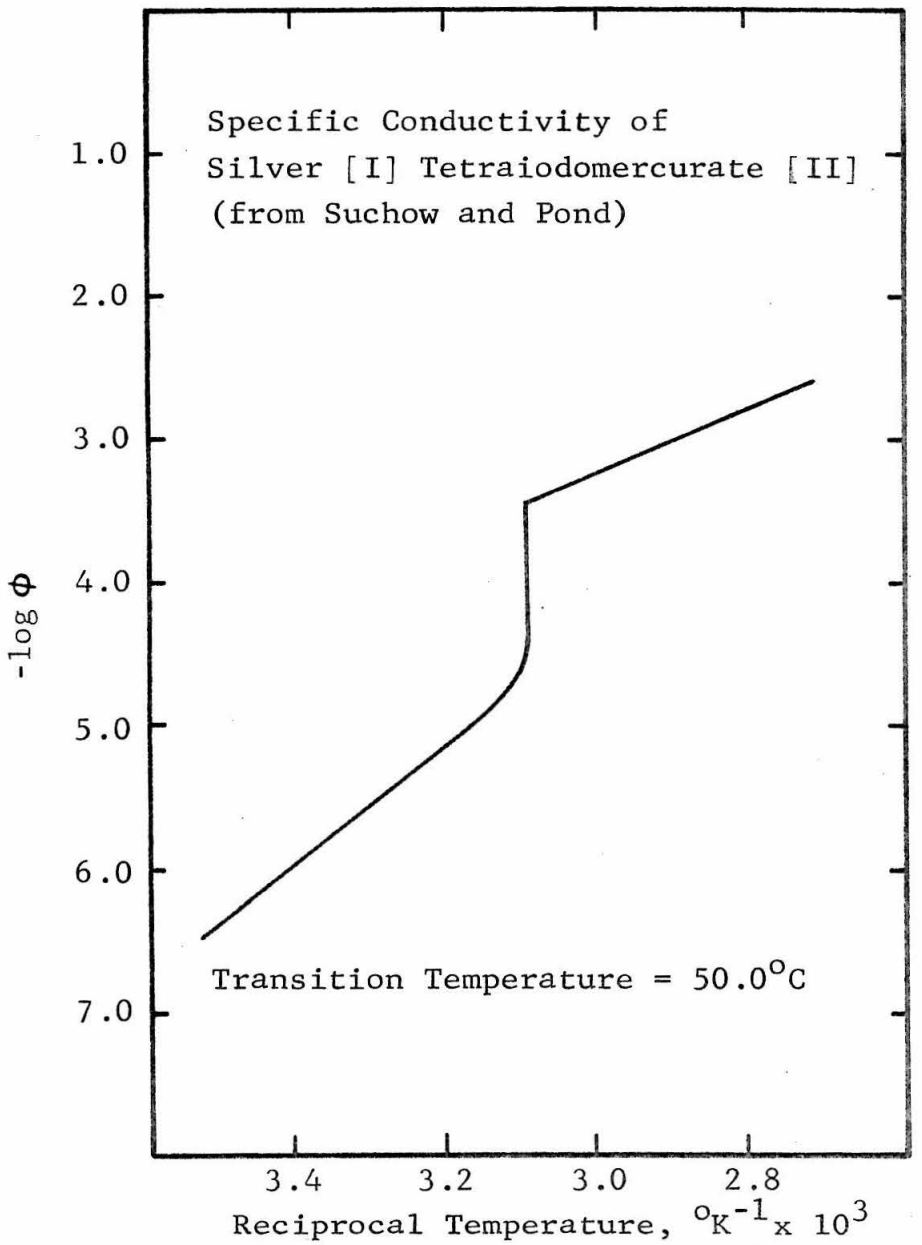

Figure 1. The Variation of Electrical Conductivity with Temperature for Silver [I] Tetraiodomercurate [II].